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(54) SOLID ELECTROLYTE MOLD, ELECTRODE MOLD AND ELECTROCHEMICAL ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid electrolyte mold and an electrode mold having superior electrochemical performance and high moldability.

SOLUTION: A hydrogenation block copolymer, which is composed of (A) a block composed of polybutadiene on which the 1,2-vinyl bond content is not more than 15% and (B) a block which is composed of butadiene 50 to 100 wt.% and the other monomer 0 to 50 wt.% and is composed of a butadiene (co) polymer on which the 1,2-vinyl bond content of a butadiene part is 20 to 90%, and is formed by hydrogenating a straight chain or a branch-shaped block copolymer on which (A)/(B) further is 5/95 to 70/30 wt.%, is used as a solid electrolyte or a binding agent of an electrode.

44 Display pole
48 Counter electrode
49 Electrolyte layer
50 Ultraviolet curing resin
51, 52 lead terminals

[Translation done.]

* NOTICES *

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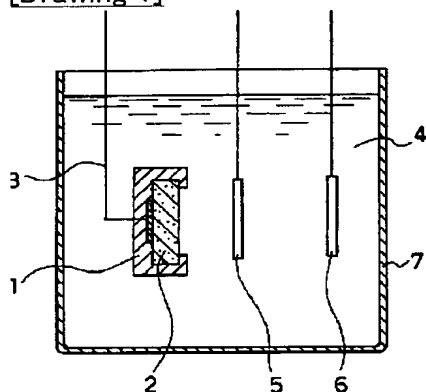
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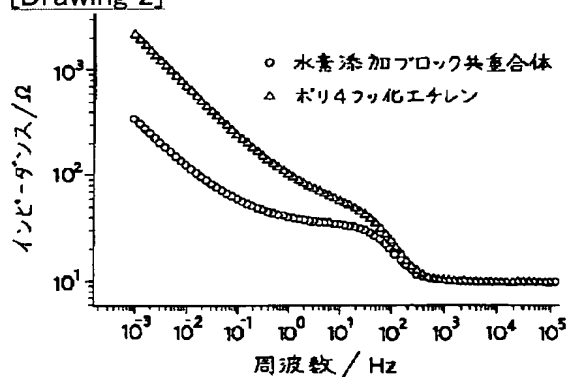
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DRAWINGS

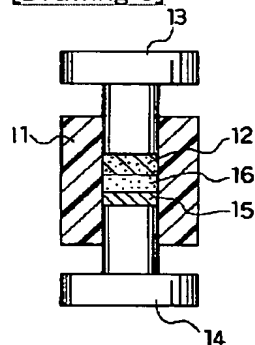
[Drawing 1]



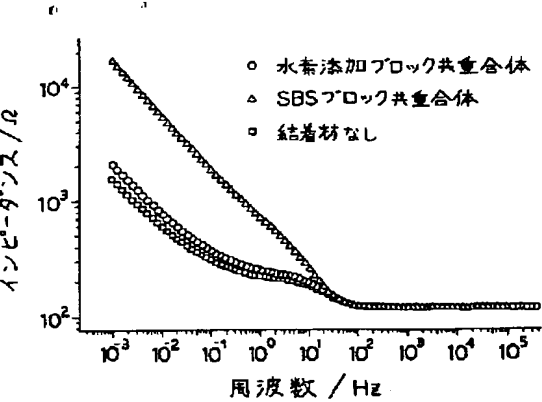
[Drawing 2]



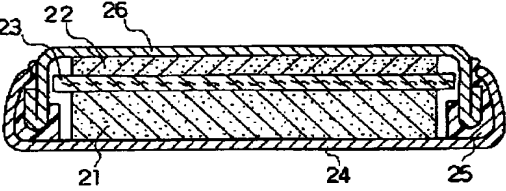
[Drawing 3]



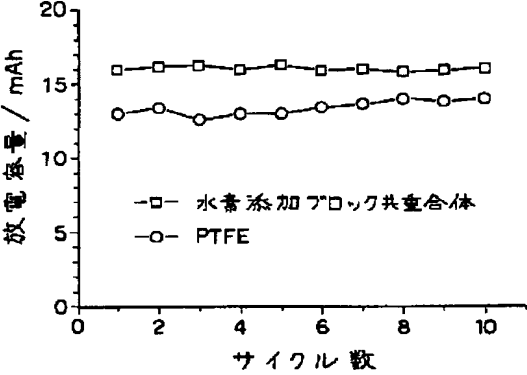
[Drawing 4]



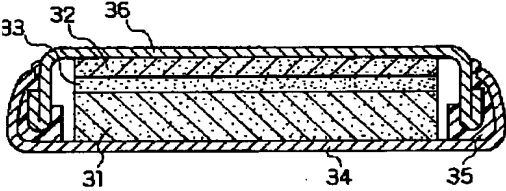
[Drawing 5]



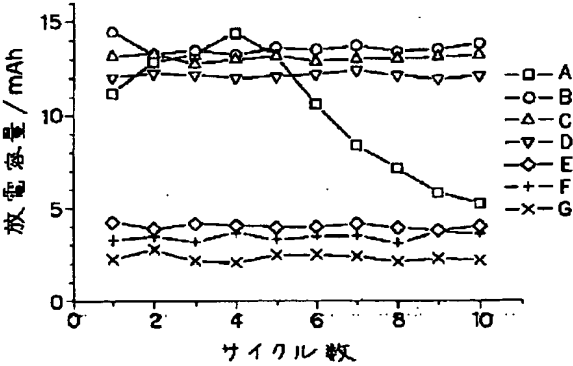
[Drawing 6]



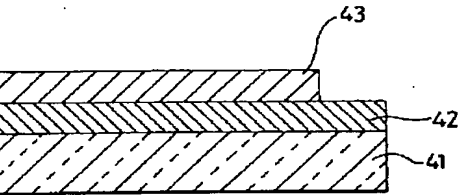
[Drawing 7]



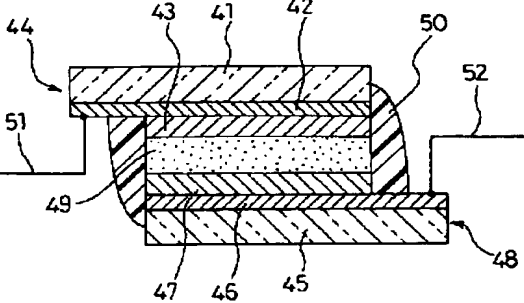
[Drawing 8]



[Drawing 9]



[Drawing 10]



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CLAIMS

[Claim(s)]

[Claim 1]A solid electrolyte molding body consisting of a hydrogenation block copolymer which was provided with the following and hydrogenated a straight chain or a branched state block copolymer which is (A)/(B) =5 / 95 to 70/30 % of the weight, and a solid electrolyte.

(A) A block with which a 1,2-vinyl bond content consists of polybutadiene which is 15% or less.

(B) A block with which it consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, and a 1,2-vinyl bond content of a butadiene part consists of a butadiene (**) polymer which is 20 to 90%.

[Claim 2]The solid electrolyte molding body according to claim 1 whose solid electrolyte is a lithium ion conductive solid electrolyte.

[Claim 3]The solid electrolyte molding body according to claim 1 whose solid electrolyte is a noncrystalline solid electrolyte.

[Claim 4]The solid electrolyte molding body according to claim 3 whose noncrystalline solid electrolyte is a lithium ion conductive solid electrolyte.

[Claim 5]The solid electrolyte molding body according to claim 4 which a lithium-ion-conductivity noncrystalline solid electrolyte makes a sulfide with a subject.

[Claim 6]The solid electrolyte molding body according to claim 5 in which a lithium-ion-conductivity noncrystalline solid electrolyte contains silicon.

[Claim 7]The solid electrolyte molding body according to claim 1 containing a structure of electronic insulation.

[Claim 8]An electrode molding body becoming considering a hydrogenation block copolymer which was provided with the following and hydrogenated a straight chain or a branched state block copolymer which is (A)/(B) =5 / 95 to 70/30 % of the weight, and an electrode active material as a subject.

(A) A block with which a 1,2-vinyl bond content consists of polybutadiene which is 15% or less.

(B) A block with which it consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, and a 1,2-vinyl bond content of a butadiene part consists of a butadiene (**) polymer which is 20 to 90%.

[Claim 9]An electrode molding body of the statement according to claim 8 in which an electrode molding body contains a lithium-ion-conductivity inorganic solid electrolyte.

[Claim 10]The electrode molding body according to claim 9 which is the noncrystalline solid electrolyte in which a lithium-ion-conductivity inorganic solid electrolyte made a sulfide a subject.

[Claim 11]The electrode molding body according to claim 8 in which an electrode molding body contains a structure.

[Claim 12]The electrode molding body according to claim 11 whose structure is electron conductivity.

[Claim 13]An electrochemical element containing a hydrogenation block copolymer which was provided with the following and hydrogenated a straight chain or a branched state block copolymer which is (A)/(B) =5 / 95 to 70/30 % of the weight.

A block which possesses an electrode and an electrolyte layer of a couple and with which at least one of an electrode of said couple and the electrolyte layers consists of polybutadiene whose (A)1,2-vinyl bond content is 15% or less.

(B) A block with which it consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other

monomers, and a 1,2-vinyl bond content of a butadiene part consists of a butadiene (**) polymer which is 20 to 90%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an electrochemical element, the solid electrolyte molding body used for this electrochemical element, and an electrode molding body. It is adding a high molecular compound in more detail to the electrolyte material which constitutes an electrochemical element, and an electrode material, and is related with the electrochemical element constituted using the molding body holding these electrochemical element component, and these molding bodies.

[0002]

[Description of the Prior Art]Electrochemical elements including a cell comprise an electrolyte layer which movement of ion produces, and an electrode layer in which transfer of the electron to ion is performed with movement of ion. A high molecular compound is added for the following purpose to these electrolyte layers and an electrode layer.

[0003][Addition to an electrolyte layer] Generally an electrolyte is the fluid in which the solvent was made to dissolve a supporting electrolyte.

Since the container which stores this fluid is needed, it is difficult to miniaturize and slim down an electrochemical element.

In order to solve this technical problem, research of all the solid electrochemical elements which replaced with the conventional liquid electrolyte and used the solid electrolyte is done. Especially as an electrochemical element, a lithium cell, Small [the atomic weight of lithium], since ionization energy is a big substance, research is briskly done as a cell which can obtain high energy density, and it has come to be broadly used as a power supply of a portable device now. A close-up of the concern about the safety of a cell has been taken by the increase in the internal energy according to the increase in the amount of content active materials along with wide use of a lithium cell on the other hand, and the increase in the content of the organic solvent which is the combustible material further used for the electrolyte in recent years.

[0004]It is very effective to replace with an organic solvent electrolyte and to use the solid electrolyte which is a noncombustible substance as a method for securing the safety of a lithium cell. Therefore, also in order to secure high safety in addition to above-mentioned miniaturization and slimming down, it is important for a lithium cell to use a solid electrolyte. As a lithium ion conductivity solid electrolyte used for such a cell, lithium halide, lithium nitride, and lithium acid matter acid chloride or these derivatives are known. $\text{Li}_2\text{S}-\text{SiS}_2$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, Lithium-ion-conductivity sulfide noncrystalline solid electrolytes, such as $\text{Li}_2\text{S}-\text{B}_2\text{S}_3$, It is known that the lithium ion conductive solid electrolyte which doped lithium salt, such as lithium halides, such as LiI , or Li_3PO_4 , on these glass shows the high ion conductivity more than $10^{-4} - 10^{-3}\text{S/cm}$. The solid polymer electrolyte which consists of organic matters is obtained by evaporating a solvent from the solution of lithium salt and an organic polymer compound to the solid electrolyte of these inorganic matter. Compared with an inorganic solid electrolyte, thin-film-izing is easy for this solid polymer electrolyte, and the solid electrolyte thin film obtained is also rich in processability, such as having flexibility.

[0005]In recent years as a solid electrolyte which has flexibility or rubber elasticity, the proposal of the new solid electrolyte named the "polymer in salt" type which consists of mineral salt which has very high-concentration lithium ion conductivity compared with the above-mentioned solid polymer electrolyte, and polymers is proposed (C. -- A. --) [Angell and] C. Liu, and E. Sanchez, Nature, and vol.632 (1993), 137. Also in the electrochemical element using a liquid electrolyte, the porous high molecular compound is usually used for the electrolyte layer as

a separator. In [excel in the water addition nature which holds a liquid electrolyte while preventing inter-electrode electronic contact mechanically, and] an electrochemical element, a separator needs to be chemically stable, and a also electrochemically stable thing is required from being used where an electrode is contacted further.

[0006][Addition to an electrode layer] An electrode comprises molding an electrode active material and making a charge collector contact. When an electrode active material is only molded by the application-of-pressure molding method, the cohesive force between electrode active material particles is mainly only Van der Waals force. However, since the usual electrochemical element uses the fluid as an electrolyte, when the electrode molding body constituted only by the application-of-pressure molding method in this way is immersed into a liquid electrolyte. The cohesive force between active material particles declines, and from an electrode molding body, an electrode active material particle drops out in a liquid electrolyte, and cannot hold shape of an electrode molding body because liquid molecules stick to an electrode active material particle surface. Therefore, in order to improve the moldability of an electrode, a high molecular compound is generally added to an electrode molding body as a binder.

[0007]To the electrolyte layer or electrode layer of an electrochemical element, although a high molecular compound is added for the above-mentioned purpose, these Prior arts have the following problem. The above-mentioned inorganic solid electrolyte is ceramics or glass.

When applying to a cell generally, it is used as a pellet which carried out application-of-pressure molding of the ground solid electrolyte powder.

However, since [with it] the pellet obtained was weak, it had the problem that it was lacking in processability and slimming down was difficult. [hard] The ionic conductivity of below 10^{-4} S/cm is [the solid electrolyte which consists of organic matters on the other hand] low at a room temperature.

As an electrolyte for lithium cells of practical use, it was insufficient.

In order to solve this problem, the proposal of the solid polymer electrolyte which improved ion conductivity is also made by adding a plasticizer. However, a plasticizer is a thing of an original inflammability and the problem of the transference number of a lithium ion falling or reactivity with a lithium anode falling generates it conversely by adding a plasticizer. and addition of a plasticizer -- it is hard to say what has performance with a solid electrolyte of these organicity sufficient as an electrolyte for lithium cells irrespective of how.

[0008]Below 10^{-4} S/cm has [the conductivity of an above-mentioned "polymer in salt" type solid electrolyte] low most.

What has ionic conductivity sufficient as an electrolyte for lithium cells cannot say.

Although high ion conductivity was shown when room temperature fused salt, such as $\text{AlCl}_3\text{-LiBr-LiClO}_4$, was used as mineral salt, it was easy to produce reduction of electrochemical aluminum, and it was not able to be said that it was suitable as an electrolyte for lithium cells.

[0009]As stated previously, an electrode molding body comprises a mixture which mixed the high molecular compound as a binder to the electrode active material. A high molecular compound is generally a thing of electric insulation.

It is easy to check movement of ion and the ionic diffusion in the electrochemical reaction produced in an electrode/electrolyte interface and also an electrode is checked.

And in order to improve moldability, when the mixture ratio of a high molecular compound was raised, it had the problem that the operational characteristic of an electrochemical element fell easily. An electrode molding body fills up with or applies to a charge collector the slurry which mixed the mixture of the electron conductive substance added if needed in carrier fluid in order to improve the electron conductivity in an electrode active material, a binder, and an electrode, and is constituted by evaporating carrier fluid. As for the high molecular compound used as a binder, in order to improve the coating nature of a slurry, and restoration nature, it is preferred that it is a thing of fusibility to the carrier fluid to be used.

[0010]When a solid electrolyte is used as an electrolyte, omission into the electrolyte of an electrode active material particle are prevented. However, in order to use an electrode molding body as an electrode active material and to only make reaction surface area into a big thing also in that case, when it is considered as the application-of-pressure molding body of the mixture which mixed the electrode active material and the solid electrolyte. The electrode molding body had the problem that it became hard weak processability with a scarce thing, and the composition of an electrochemical element will become difficult. Since a contact interface with an electrode active material turns into an interface of a solid/solid when a solid electrolyte is used as an electrolyte,

compared with the case where a liquid electrolyte is used, it becomes what has a small touch area of an electrode active material and an electrolyte. Therefore, the tendency used as a big thing has electrode reaction resistance. In order to improve moldability, the tendency becomes still more remarkable when the high molecular compound of electric insulation is added. Therefore, it had the problem that an electrode reaction rate fell easily. If a lithium cell is mentioned as an example of an electrochemical element, as an electrode active material, a lithium cobalt oxide (Li_xCoO_2) will be used for an anode, and black lead etc. will be used for a negative electrode, respectively. When it used for the lithium cell as an electrode molding body by which application-of-pressure molding was carried out as stated also in advance since these were obtained as powder, the electrolyte of the fluid invaded among electrode configuration particles, the electrode swelled, and maintaining shape had the problem that electric contact was also easy to be lost difficult. Li_xCoO_2 has the structure in which the triangular lattice of oxygen, lithium, and cobalt was piled up in order of O-Li-O-Co-O-Li-O. A lithium ion exists between the layers of CoO_2 .

A lithium ion goes in and out between CoO_2 layers by the electrochemical oxidation-reduction reaction in the inside of a lithium ion conductivity electrolyte. As a result, the size of the electric interaction between CoO_2 layers changes, elasticity arises between layers, and a volume change arises in an electrode. Therefore, whenever it repeated charge and discharge, the junction between the particles which constitute an electrode was easy to be lost, and it had a problem of capacity falling in connection with a charging and discharging cycle.

[0011]As mentioned above, although Li_xCoO_2 was explained as an electrode active material, As an active material in which application of the substance conventionally used as an active material for lithium cells or future is expected, Transition metal bisulfides, such as transition metal oxides, such as Li_xNiO_2 , Li_xMnO_2 , and MnO_2 , and Li_xTiS_2 , or a graphite lamellar compound, graphite fluoride, etc. are mentioned. Also when such materials are used, the same problem arises. When a solid electrolyte is used as an electrolyte, it is in the tendency which becomes what has a small touch area between a solid electrolyte and an electrode active material as stated also in advance. Therefore, when the volume change of the electrode active material accompanying the charge and discharge of a cell arises, junction between an active material and an electrolyte is easier to be lost. Since the elastic body which absorbs the volume change of an electrode active material in the case of charge and discharge does not exist in the inside of a cell as a result of all the battery materials' comprising a hard solid, there is a possibility that change of battery size and poor obturation of the cell obturation part accompanying this may arise.

[0012]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the solid electrolyte molding body which solves the above technical problem, shows outstanding electrochemical characteristics including high ion conductivity, has flexibility further, and was excellent in processability. Another purpose of this invention is to provide the electrode molding body which could constitute the electrochemical element which shows the outstanding operational characteristic, and was excellent in moldability and processability. The further purpose of this invention is to provide the electrochemical element which solves the technical problem resulting from the volume change of the electrode active material under operation of these electrochemical elements, and stabilizes and operates.

[0013]

[Means for Solving the Problem]A block with which a solid electrolyte molding body of this invention consists of polybutadiene whose (A)1,2-vinyl bond content is 15% or less, (B) It consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, And a 1,2-vinyl bond content of a butadiene part consists of a block which consists of a butadiene (**) polymer which is 20 to 90%, And it consists of a hydrogenation block copolymer produced by hydrogenating a straight chain or a branched state block copolymer which is (A)/(B) = 5 - 70 / 95 to 30 % of the weight, and a solid electrolyte. An electrode molding body of this invention comprises an electrode active material and an aforementioned hydrogenation block copolymer. An electrochemical element of this invention possesses an electrode and an electrolyte layer of a couple, and considers at least one of an electrode of said couple, and the electrolyte layers as composition containing the above-mentioned hydrogenation block copolymer.

[0014]A hydrogenation block copolymer which is one of the main ingredients of this invention, A polybutadiene block (A) whose 1 and 2-vinyl bond content is 15% or less. It consists (it is hereafter called the block A) of at

least one piece, 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, And a butadiene (**) polymer whose 1,2-joint content of a butadiene part is 20 to 90%. A straight chain whose rates of the block A in a molecule and the block B it has at least one (it being hereafter called the block B), and are 5-70/95-30 (% of the weight), or a branched state block polymer. It is a hydrogenation block polymer produced by carrying out hydrogenation of (calling it a non-hydrogenated block polymer hereafter) not less than 90%. The block A turns into crystalline polyethylene similar structure blocks by hydrogenation, and the block B of a hydrogenation block polymer turns into a rubber-like block of an olefin skeleton.

[0015]Here, a lithium ion conductive solid electrolyte is used as a solid electrolyte of a solid electrolyte molding body. A noncrystalline solid electrolyte is used as a solid electrolyte. As a lithium ion noncrystalline solid electrolyte, a thing which makes a sulfide a subject, especially a thing containing silicon are used suitably. The solid electrolyte molding body can contain a structure of electronic insulation.

[0016]As for an electrode molding body, it is preferred that a lithium-ion-conductivity inorganic solid electrolyte is included. As a lithium-ion-conductivity inorganic solid electrolyte, an amorphous thing which made a sulfide a subject is used suitably. As for an electrode molding body, it is preferred that a structure is included, and thing of a structure of electron conductivity is more preferred.

[0017]

[Embodiment of the Invention]This invention persons by using the hydrogenation block copolymer which has crystalline polyethylene similar structure blocks and the rubber-like block of an olefin skeleton as a high molecular compound, Movement of the ion between the substances which constitute electrochemical elements, such as an electrode active material / electrolyte interface, is made easy between inorganic solid electrolyte particles and between electrode active material particles, high moldability and flexibility are given to a solid electrolyte molding body, an electrode molding body, etc., and it is based on having found out that processability could be improved. For example, if a high molecular compound is mixed in order to give flexibility to an inorganic solid electrolyte, the surface of inorganic solid electrolyte particles will be in the state where it was covered with the insulating high molecular compound. As a result, the ion conduction between solid electrolyte particles is checked, and the ionic conductivity of the complex of the ion-conductive inorganic solid electrolyte obtained and a high molecular compound will become low. By however, the thing for which the hydrogenation block polymer which has the crystalline polyethylene similar structure blocks and the rubber-like block of an olefin skeleton by this invention is used as a high molecular compound. Without spoiling high ion conductivity greatly, the binding property between solid electrolyte particles can be improved, and flexibility etc. can be given to the molding body of a solid electrolyte. By introducing crystalline polyethylene similar structure blocks, the hydrogenation block copolymer of this invention is that a little addition can also give flexibility, and can obtain the lithium-ion-conductivity molding body which has high conductivity.

[0018]It explains to details per this invention below. The 1,2-vinyl bond content of the block A before hydrogenation is an important factor which determines the cohesive force of the melting point resulting from the block A, and polyethylene similar structure blocks after hydrogenation. If especially cohesive force declines, it becomes impossible to lessen an addition and a high lithium-ion-conductivity complex cannot be obtained. 1 of the block A and 2-vinyl bond content need to be 15% or less. If 1 of the block A and the amount of 2-vinyl bonds exceed 15%, the cohesive force of the block A after hydrogenation declines, and it is not desirable, and since the melting point also falls, heat resistance also falls and it is not desirable. The block B before hydrogenation consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, and the 1,2-vinyl bond content of a butadiene part is a block segment which consists of a butadiene (**) polymer which is 20 to 90%, and it turns into a block like rubber by hydrogenation. In the block B, since 1 of a butadiene part and 2-vinyl bond content serve as butene structure by hydrogenation, the content has direct influence on the glass transition temperature resulting from the block B after hydrogenation, and serves as a factor which influences flexibility in a complex with a lithium ion conductive solid electrolyte.

[0019]In this invention, 1 of the block B and 2-vinyl bond content need to be not less than 20% and 90% or less. It is not desirable, in order that an after-hydrogenation crystallinity portion may arise and 1 of the block B and 2-vinyl bond content may reduce flexibility in less than 20%. If 90% is exceeded, in order for a butene content to increase too much and to raise glass transition temperature, since flexibility is reduced, it is not desirable. As butadiene in the block B, and other copolymerizable monomers, although acrylic ester (meta), such as aromatic vinyl compounds, such as styrene, alpha-methylstyrene, and ****- methylstyrene, methyl methacrylate, and methyl acrylate, isoprene, etc. are mentioned, Especially styrene and isoprene are preferred. The amount of these monomers used is 0 to 50% of total monomers which constitute the block B. If 50% is exceeded when using other

monomers, since the flexibility after hydrogenation falls, it is not desirable. In the block copolymer before hydrogenation, it may have a polymeric block (henceforth the block X) which is mainly concerned with an aromatic vinyl compound.

[0020]The hydrogenation block copolymer of this invention is a hydrogenation block copolymer produced by hydrogenating at least one block A, at least one block B, the straight chain that has the block X if needed further, or a branched state block copolymer. a non-hydrogenation block copolymer -- concrete -- $A-(B-A)_l$ and $_m(A-B)$ (1 or more [However, l and m]) -- or $(A-B-X)_n$ (1 or more [However, n]) -- it is shown by the structural formula. In the block copolymer which has such a structure, an A-B-A type triblock copolymer and the triblock copolymer of an A-B-X (X is polystyrene block) mold are preferred.

[0021]The ratios of the block A and the block B occupied in a non-hydrogenation block copolymer are block A / block B = 5-70 / 95 to 30 % of the weight. Since crystalline block segments run short when the block B exceeds 95 % of the weight at less than 5 % of the weight in the block A of a non-hydrogenation block copolymer, cohesive force cannot decline and high moldability cannot be obtained in the range with few additions to a solid electrolyte. When the block A is [the block B] less than 30 % of the weight exceeding 70 % of the weight, the hardness of a hydrogenation copolymer rises and flexibility is spoiled. the ratio of the block X occupied in a non-hydrogenation block copolymer when a non-hydrogenation block copolymer is a $_n(A-B-X)$ type -- usually -- it is 30 or less % of the weight still more preferably 40 or less % of the weight preferably 50 or less % of the weight. Since the pliability of a hydrogenation block copolymer will fall if the block X exceeds 50 % of the weight, the flexibility of a solid electrolyte molding body falls. As for the ratio of the block A and the block B, it is desirable that it is within the limits of the above-mentioned in the portion except the block X. The hydrogenation rate of the block copolymer after hydrogenation needs to be not less than 90%. The melting point falls [a hydrogenation rate] at less than 90%, and heat resistance falls.

[0022]A hydrogenation block copolymer has the feature that the melting point which originates in the block A after hydrogenation at the elevated-temperature side, and the glass transition point which originates in the block B after hydrogenation at the low temperature side are shown. The melting point of a hydrogenation block copolymer is a factor which carries out a direct action to the heat resistance of the constituent of this invention, and is not less than 80 ** usually not less than 95 ** especially preferably not less than 85 ** preferably. In the melting point below 80 **, the heat resistance of a constituent is inferior and it becomes a problem practically. Although the maximum of the service temperature of an element is restricted by the boiling point of the electrolyte used in the usual electrochemical element, in the case of the electrochemical element using the solid electrolyte as an electrolyte, the maximum of such service temperature will become higher. Since the activation energy of conduction of a solid electrolyte is generally high compared with the thing of a liquid electrolyte, at an elevated temperature, movement of the ion in an electrolyte will become quick and the electrochemical element using a solid electrolyte will show the characteristic which excelled what used the liquid electrolyte in the elevated temperature. Therefore, it is required for the heat resistance of the high molecular compound used to be high. In the case of the fuel cell using a proton conductivity solid electrolyte, etc., the temperature of an element may be about 100 ** by generation of heat under operation of an element. Therefore, as for the melting point of a hydrogenation block copolymer, it is more preferred that it is not less than 95 **. moreover -- the glass transition temperature by the side of the low temperature of a hydrogenation block copolymer is a factor which acts on the low-temperature characteristic of a constituent -- usually -25 ** or less -30 ** or less is -35 ** or less especially preferably preferably. When the glass transition temperature by the side of low temperature exceeds -25 **, the kinetic property at the time of low temperature declines, and decline in the ionic conductivity by the side of the low temperature of a constituent also becomes large.

[0023]A hydrogenation block copolymer can be manufactured with a known technique. For example, it can manufacture by the method currently indicated by JP,4-342752,A. As a solid electrolyte in which the ion conductivity more than 10^{-4} S/cm is shown at a room temperature, the thing of copper-ion conductivity, silver ion conductivity, proton conductivity, and fluoride ion conductivity, etc. are found out until now. The lithium ion conductivity solid electrolyte attracts attention as an electrolyte for all the solid lithium cells especially. However, the lithium cell which generates high tension is equipped with the anode in which strong oxidizing power is shown, and the negative electrode in which strong reducing power is shown. Therefore, movement of ion is not barred, but even if the high molecular compound added by the electrolyte layer shows the characteristic which shows a high binding property, it may deteriorate by contact with these anodes or a negative electrode. The effect is the

largest when the hydrogenation block copolymer by this invention constitutes a solid electrolyte molding body with a lithium ion conductivity solid electrolyte, since it is stable also to such an oxidation-reduction reaction. [0024]When a lithium ion conductivity thing is taken for an example, a solid electrolyte The thing of crystalline substances, such as $\text{Li}_{1.3}\text{Sc}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ and $\text{Li}_{0.2}\text{La}_{0.6}\text{TiO}_3$. It is divided roughly into amorphous things, such as $\text{Li}_2\text{S}-\text{SiS}_2$. The thing of a crystalline substance has many which have anisotropy in the conductivity of ion, in order to realize high ion conductivity, it sinters a molding body, and the necessity of connecting an ion conduction course between solid electrolyte particles often produces it. To it, the ion conduction of a noncrystalline solid electrolyte is isotropic, and the ion conduction course between particles can be easily connected by the application-of-pressure molding method. Therefore, in the solid electrolyte molding body aiming at simplifying the composition process in constituting an electrochemical element, it is preferred to use an amorphous solid electrolyte. There are some which make a subject oxides, such as what makes sulfides, such as $\text{Li}_2\text{S}-\text{SiS}_2$, a subject, and $\text{Li}_2\text{O}-\text{SiO}_2$, in a lithium ion conductivity noncrystalline solid electrolyte. What makes a sulfide a subject has high reactivity, such as moisture, and also when mixing with a high molecular compound, there are the necessity of using the solvent of non-polarity etc. It is meltable to the solvent of non-polarity, and the hydrogenation block copolymer in this invention can be composite-ized, without spoiling the characteristic of the lithium-ion-conductivity noncrystalline solid electrolyte which made the sulfide the subject. [0025]As a lithium-ion-conductivity inorganic solid electrolyte, high ion conductivity and the thing which has a large potential window are preferred, and especially the amorphous thing that made the sulfide the subject is preferred as what has these characteristics. As a lithium-ion-conductivity amorphous inorganic solid electrolyte which made the sulfide the subject, when a lithium sulfide and a silicon sulfide are made into the charge of a start material, it becomes what has the low steam pressure of the charge of a start material, and evapotranspiration of the charge of a start material at the time of solid electrolyte composition can be suppressed. Therefore, since the synthetic method of a solid electrolyte can be made simple, as a lithium-ion-conductivity amorphous inorganic compound, the thing containing silicon is used especially preferably. The mechanical strength of a lithium ion conductive solid electrolyte molded body can be further raised by adding the structure of electronic insulation. As an example of the structure of electronic insulation, textile fabrics, a nonwoven fabric, a porous film, etc. can be mentioned. As a method of manufacturing the solid electrolyte Plastic solid of this invention, the solution of a hydrogenation block copolymer is added to solid electrolyte powder, mixture dispersion is performed with a paint conditioner etc., and the slurry which solid electrolyte powder distributed in the solution of a hydrogenation block copolymer is obtained. Subsequently, the method of carrying out coating of the slurry on a substrate with a mold-release characteristic, and acquiring the solid electrolyte Plastic solid of film state or the method of applying or impregnating electronic insulation structures, such as textile fabrics, with a slurry, and acquiring a sheet shaped solid electrolyte Plastic solid is mentioned. [0026]Without barring movement of ion, when it composite-izes with other particles, the hydrogenation block copolymer by this invention can make the binding property between particles good, and can obtain a molding body with high processability. In the electrode used for an electrochemical element, an exchange of ion is performed between an electrode active material and an electrolyte. Since it is necessary to give high moldability to an electrode, without barring a motion of ion as stated previously, the electrode molding body which can be satisfied with using the hydrogenation block copolymer by this invention of these requests can be constituted. When a solid electrolyte is used as an electrolyte, in order to improve moldability, as it especially said previously that a binder is added, it has a problem to which an electrode reaction rate falls easily, and especially the effect using a hydrogenation block copolymer as a binder is large. The effect of using especially a hydrogenation block copolymer will become big from the anti-oxidation reduction nature of a binder becoming important as stated also in advance as an electrode active material in the case of the active material for lithium cells. In that case, an electrode molding body contains an electrode active material or an electrode active material, and a solid electrolyte, and the solid electrolyte used is a lithium ion conductivity thing. Since there is nothing amorphous in an ion conduction course as a lithium ion conductive solid electrolyte as for anisotropy, connection of the ion conduction course between an electrode active material and an electrolyte becomes easy. As an amorphous lithium ion conductive solid electrolyte, what made the sulfide the subject is especially used preferably from high ion conductivity and a large potential window being shown. [0027]The mechanical strength of an electrode molding body can be further raised by adding a structure to an electrode molding body. Since electron conductivity inside an electrode can be made high especially as a

structure, the structure which consists of an electron conductive substance is used especially preferably. Here, as an example of the structure which consists of an electron conductive substance which can be used, there are metallic meshes, such as stainless steel, titanium, copper, etc. The hydrogenation block copolymer used for this invention has the rubber-like block of an olefin skeleton with crystalline polyethylene similar structure blocks. Since the rubber-like block of an olefin skeleton has big free volume, it can absorb the volume change of the electrode active material under operation of an electrochemical element. Since crystalline polyethylene similar structure blocks give a binding property and flexibility strong between the constituent particles of an electrochemical element, the electrochemical element which solves the problem resulting from the fall of the junction nature between the particles by the volume change of an active material, and stabilizes and operates can be obtained.

[0028]

[Example] Hereafter, the example of this invention is described in detail. All of composition of the lithium-ion-conductivity inorganic solid electrolyte explained below and its ionic conductivity measurement were performed under dry argon atmosphere. First, the synthetic example of a hydrogenation block copolymer is explained. The structure and the characteristic of a hydrogenation block copolymer are shown in Table 1. A in the structural formula of an ingredient shows the block A among front, B shows the block B, and X shows a polystyrene block, respectively. A manufacturing method is shown below. [0029] [Manufacture of a hydrogenation block copolymer (H-1)] 3.2 kg of cyclohexane and 1.2 kg of butadiene are taught to the autoclave of 20 l. of inner capacity, and 33 ml of 14-% of the weight tetrahydrofuran solutions of n-butyl lithium are added. Temperature up is carried out to about 70 **, 2.8 kg of butadiene and 108 ml of tetrahydrofurans are added further in the place where the appending rate became 100%, and a polymerization is continued at about 70 **. 26 ml adding and making the 20-% of the weight tetrahydrofuran solution of dichlorosilane react for about 20 minutes, when an appending rate will be 100% -- a jib -- coupling of the lock polymer was carried out and the triblock copolymer was obtained. After a polymerization is completed, reaction mixture shall be 70 ** and The n-butyl lithium 3g, 3 g of 2,6-di-t-butyl-p-cresol, 1g of bis(cyclopentadienyl)titanium dichloride, and 2 g of diethylaluminum chloride were added, and it was made to react by 10kg/cm of hydrogen pressure ² for 1 hour. This reaction mixture was dried with a roll after a steam strip, and the hydrogenation block copolymer (H-1) was obtained.

[A hydrogenation block copolymer (H-2) - (H-4) manufacture] So that it may become each hydrogenation block copolymer as shown in Table 1, Monomer species, a monomer amount, a catalyst amount, polymerization temperature, polymerization time, etc. were changed, and hydrogenation block copolymer (H-2) - (H-4) was obtained according to the hydrogenation block copolymer (H-1).

[0030]

[Table 1]

試料番号	H-1	H-2	H-3	H-4
成分の構造式	A-B-A	A-B-A	A-B-A	A-B-X
ブロック A の 1,2-ビニル結合含量(%)	12	13	12	13
ブロック A 量(重量%)	30 (15×2)	20 (10×2)	40 (20×2)	15
ブロック B の 1,2-ビニル結合含量(%)	42	41	65	42
ブロック B 量(重量%)	70	80	60	70
ブロック X 量(重量%)				15
特性				
水素添加率(%)	98	97	98.5	97.5
融点(高温側)	92	89	90	92
ガラス転移温度(低温側)	-52	-54	-55	-51
MFR(230℃×2.16kg)	10	5	8	0.5
分子量(×10 ⁴)	15	20	15	15

[0031]<<Example 1>> -- the sulfide glass of the lithium ion conductivity expressed with 0.6Li₂S-0.4SiS₂ as a solid electrolyte -- the lithium ion conductive solid electrolyte molded body was obtained, using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by 0.6Li₂S-0.4SiS₂ as a solid electrolyte was compounded. The silicon sulfide (SiS₂) was mixed with the lithium sulfide (Li₂S) at a rate of 0.6:0.4 by the mole ratio, and the mixture was put in the crucible of glassy carbon. The crucible was put in the vertical type furnace, it heated to 950 ** in the argon air current, and the mixture was made into the molten state. After 2-hour heating, crucible was dropped into liquid nitrogen, and was quenched, and the lithium-ion-conductivity noncrystalline solid electrolyte expressed with 0.6Li₂S-0.4SiS₂ was obtained. Thus, from the lithium-ion-conductivity noncrystalline solid electrolyte and hydrogenation block copolymer (H-1) which were obtained, the lithium ion conductive solid electrolyte molded body was obtained by the following method. First, the solid electrolyte obtained above was ground to 350 or less meshes. The toluene solution of (H-1) was added to this solid electrolyte powder, and it fully kneaded, and was considered as slurry form. It was made for the solid content of a hydrogenation block copolymer and the weight ratio of solid electrolyte powder to be set to 2:98 as for the mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the lithium ion conductive solid electrolyte molded body was obtained.

[0032]The ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the alternating-current-impedance method described below. First, the sheet of the lithium ion conductive solid electrolyte molded body obtained above was clipped to the discoid of 10 mmphi. The platinum board of 10 mmphi was welded by pressure to both sides of this disk, it was considered as the electrode for impedance measurement, and the ionic conductivity measuring cell was constituted. Alternating current impedance impressed and measured the volts alternating current of 10 mV with the vector impedance analyzer. As a result, the ionic conductivity of the obtained lithium ion conductive solid electrolyte molded body was 2.45x10⁻⁴S/cm.

When the hydrogenated block copolymer was not added as a comparative example, but pressing of the solid electrolyte powder was carried out and the ionic conductivity was measured similarly, it was $4.5 \times 10^{-4} \text{ S/cm}$. Next, the bending test was done in order to investigate that flexibility as evaluation of the processability of this lithium ion conductive solid electrolyte molded body. The bending test twisted this lithium ion conductive solid electrolyte molded body around the Indanthrene loess reinforcing bars of 50 mmphi, and viewed the state of the molding body. As a result, as for the lithium ion conductive solid electrolyte molded body in this example, it turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test. As mentioned above, it turned out that it has high lithium ion conductivity according to this invention, and the lithium ion conductive solid electrolyte molded body excellent in processability is obtained.

[0033]<<Example 2>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-2), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $2.8 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0034]<<Example 3>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-3), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $3.4 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0035]<<Example 4>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-4), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $2.5 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0036]<<Example 5>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-3) was used for Example 3 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte was compounded. First, the glass preform for compounding a noncrystalline solid electrolyte was compounded. The silicon sulfide (SiS_2) was mixed with the lithium sulfide (Li_2S) at a rate of 0.64:0.36 by the mole ratio, this mixture was put in glassy carbon crucible, and it fused at 950 ** among the horizontal type furnace. Then, the noncrystalline solid electrolyte which quenches melt with a congruence roller and is expressed with $0.64\text{Li}_2\text{S}-0.36\text{SiS}_2$ was obtained. This noncrystalline solid electrolyte was made into the glass preform, and lithium phosphate was mixed so that it might become the presentation of $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ after grinding. The lithium-ion-conductivity noncrystalline solid electrolyte which heats and quenches this mixture by the same method as the above, and is expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ was obtained.

[0037]0. replacing with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and using this solid electrolyte -- as a hydrogenation block copolymer -- Example 3 -- having used (H-3) -- the lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having used. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $5.3 \times 10^{-4} \text{ S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $7.8 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0038]<<Example 6>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.05\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-3) was used for Example 3 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. 0. The lithium-ion-conductivity noncrystalline solid

electrolyte expressed with $0.5\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ was compounded by the same method as Example 5 except having replaced with lithium phosphate and having used lithium oxide. using the obtained lithium ion conductive solid electrolyte -- as a hydrogenation block copolymer -- Example 3 -- having used (H-3) -- the lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having used. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $4.3 \times 10^{-4}\text{S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $6.6 \times 10^{-4}\text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0039]<<Example 7>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte was compounded. First, the noncrystalline solid electrolyte expressed with the same method as Example 1 by $0.5\text{Li}_2\text{S}-0.5\text{SiS}_2$ was obtained except having changed the mixture ratio of the starting material. This noncrystalline solid electrolyte was made into the glass preform, and after grinding, lithium iodide was mixed so that it might become the presentation of $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$. The lithium-ion-conductivity noncrystalline solid electrolyte which heats and quenches this mixture in a similar way again, and is expressed with $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ was obtained.

[0040]0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and having used this solid electrolyte. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $3.5 \times 10^{-4}\text{S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $7.2 \times 10^{-4}\text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also to the bending test done by the same method as Example 1.

[0041]<<Example 8>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the phosphorus sulfide (P_2S_5) was mixed with the lithium sulfide (Li_2S) at a rate of 0.5:0.5 by the mole ratio as raw material of a solid electrolyte. This mixture was enclosed in the quartz tube, at 900 **, the quartz tube was dropped underwater, and was quenched after melting, and the noncrystalline solid electrolyte expressed with $0.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5$ was obtained. 0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and having used this solid electrolyte. The place which measured the ionic conductivity of the solid electrolyte powder which is this lithium ion conductive solid electrolyte molded body and a comparative example by the same method as Example 1, The ionic conductivity of the solid electrolyte molding body which added the hydrogenation block copolymer is $1.0 \times 10^{-4}\text{S/cm}$, and the fall rate had fitted in less than 1/2 as compared with solid electrolyte independent $1.6 \times 10^{-4}\text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also to the bending test done by the same method as Example 1.

[0042]<<Example 9>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{B}_2\text{S}_3$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, as raw material of a solid electrolyte, The noncrystalline solid electrolyte expressed with the same method as Example 8 by $0.6\text{Li}_2\text{S}-0.4\text{B}_2\text{S}_3$ was obtained except having used

what mixed boron sulfide (B_2S_3) with the lithium sulfide (Li_2S) at a rate of 0.6:0.4 by the mole ratio. 0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6Li_2S-0.4SiSB_2$, and having used this solid electrolyte. The place which measured the ionic conductivity of the solid electrolyte powder which is this lithium ion conductive solid electrolyte molded body and a comparative example by the same method as Example 1, The ionic conductivity of the solid electrolyte molding body which added the hydrogenation block copolymer is $1.2 \times 10^{-4} S/cm$, and the fall rate had fitted in less than 1/2 as compared with solid electrolyte independent $1.9 \times 10^{-4} S/cm$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0043]<<Example 10>> the noncrystalline solid electrolyte expressed with $0.6Li_2S-0.4SiS_2$ like Example 1 as a lithium ion inorganic solid electrolyte, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium-ion-conductivity inorganic solid electrolyte and a hydrogenation block copolymer were obtained using (H-3) as a hydrogenation block copolymer. The details are shown below. From the lithium-ion-conductivity inorganic solid electrolyte obtained in Example 1, and (H-3), the lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained. the composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are boiled and shown in Table 2. The result of a bending test is also shown in Table 2.

[0044]
[Table 2]

共重合体比率 (wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4} S/cm$)	4.1	3.8	3.4	2.8	2.0
折り曲げ試験	良好	良好	良好	良好	良好
注			実施例 3		

[0045]It turns out that it excels in flexibility and the lithium ion conductive solid electrolyte molded body whose ionic conductivity is also very high is simultaneously obtained also with a little additions by using a hydrogenation block copolymer from this result. Even if it adds a hydrogenation block copolymer comparatively so much, the fall of ionic conductivity also has the small feature.

[0046]<<Example 11>> the noncrystalline solid electrolyte expressed with $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$ obtained in Example 5 as a lithium-ion-conductivity inorganic solid electrolyte, The lithium ion conductive solid electrolyte molded body was obtained using a polyethylene mesh as a structure of further electronic insulation using (H-3) respectively as a hydrogenation block copolymer. The details are shown below. The slurry containing a solid electrolyte and a specific polymer was obtained by the same method as Example 1. Then, with the doctor blade method, the opening of the polyethylene mesh of 70% of a numerical aperture was filled up with this slurry. Then, it dried under decompression of 40 **, toluene was evaporated, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $3.0 \times 10^{-4} S/cm$. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen as for an exterior, and abnormalities are not seen by the bending test using the stainless steel stick of 5 more mmphi, either, but the lithium ion conductor by this example has higher flexibility. As mentioned above, according to this invention using a lithium-ion-conductivity inorganic

solid electrolyte, a hydrogenation block copolymer, and the structure of further electronic insulation, it turned out that it has high processability and a lithium ion conductive solid electrolyte molded body with high lithium ion conductivity is obtained especially.

[0047]<<Example 12>> as a lithium-ion-conductivity inorganic solid electrolyte. The lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ which was replaced with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ used in Example 11, and was obtained in Example 1, moreover -- as a hydrogenation block copolymer -- Example 11 -- having used (H-3) -- replacing with (H-1) -- it using, respectively and, The lithium ion conductive solid electrolyte molded body consisted of the same methods as Example 11 except having replaced with the polyethylene mesh used in Example 11, and having used the mesh of glass fiber as an electronic insulation structure. When the ionic conductivity of the lithium ion conductive solid electrolyte molded body obtained as a result was measured like Example 1, it was $3.3\times 10^{-4}\text{S/cm}$. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen as for an exterior, and abnormalities are not seen by the bending test using the stainless steel stick of 5 more mmphi, either, but it has flexibility with a higher lithium ion conductive solid electrolyte molded body by this example.

[0048]<<the comparative example 1>> -- the styrene ethylene butylene styrene block copolymer (the product made from SHELL.) which does not have a crystalline block structure It expresses with trade name KRATON G1652 and the following SEBS. It uses, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium ion electrical transmission nature inorganic solid electrolyte and SEBS were obtained using the noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ like Example 1 as a lithium-ion-conductivity inorganic solid electrolyte. The details are shown below. The lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained from the lithium-ion-conductivity inorganic solid electrolyte obtained in SEBS and Example 1. The composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are shown in Table 3. The result of a bending test is also shown in Table 3.

[0049]
[Table 3]

SEBS 共重合体比率 (wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4}\text{S/cm}$)	—	—	—	0.9	0.5
折り曲げ試験	成型体として回収不可	成型体として回収不可	成型体として回収不可	ひび割れ発生	良好
注	成型体として回収不可のため伝導度測定不可				

[0050]<<Comparative example 2>> 5 % of the weight of styrene and 95 % of the weight of butadiene are polymerized, The copolymer (it expresses with H-SBR below.) produced by the 1,2-vinyl bond content of butadiene hydrogenating the styrene butadiene random copolymer which is 80% is used, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium-ion-conductivity inorganic solid electrolyte and H-SBR were obtained using the noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ like Example 1 as a lithium ion inorganic solid electrolyte. The details are shown below. The lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained from the lithium-ion-conductivity inorganic solid electrolyte obtained in H-SBR and Example 1. The composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are shown in Table 4. The result of a bending test is also shown in Table 4.

[0051]
[Table 4]

H-SBR 比率(wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4}$ S/cm)	—	—	—	—	0.4
折り曲げ試験	成型体として回収不可	成型体として回収不可	成型体として回収不可	成型体として回収不可	良好
注	成型体として回収不可のため伝導度測定不可				

[0052]When processability is good, and is rich in flexibility and the hydrogenation block copolymer of this invention which has a crystalline block obtains the lithium ion conductive solid electrolyte molded body of high ion conductivity by comparison with the above example and a comparative example, it turns out that it is a suitable material.

[0053]<<Example 13>> In this example, the proton conductivity solid electrolyte molding body was produced, using (H-1) respectively as the silica gel which doped phosphoric acid as a solid electrolyte of proton conductivity, and a hydrogenation block copolymer. First, the silica gel which doped phosphoric acid was compounded by the following methods. It diluted with ethanol, using a tetraethoxysilane (it expresses with the following TEOS.) as a starting material for compounding silica gel. It was made for the mixture ratio of TEOS and ethanol to be set to 1:4 by a mole ratio at this time. In this solution, it is a rate of 8 and 0.01 in the mole ratio to TEOS, respectively, and in addition, pure water and tetraethylammonium tetrafluoroborate were stirred for 5 minutes so that a 3.6wt% hydrochloric acid aqueous solution might be set to 0.01 by the mole ratio of HCl to TEOS. Then, the 85wt% phosphoric acid aqueous solution was added so that it might be set to TEOS:H₃PO₄=1:0.5, and it stirred in the well-closed container for 3 hours. Subsequently, it was neglected for 5 hours, gelled, it heated at 150 ** for 2 hours, and the silica gel which doped phosphoric acid was obtained.

[0054]The silica gel which doped the phosphoric acid obtained as mentioned above was ground, and it stirred in the toluene solution of (H-1). However, it was made for the ratio of the solid electrolyte of proton conductivity to the solid content of a copolymer (H-1) to be set to 19:1 by a weight ratio. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, it dried under decompression of 100 **, and toluene was evaporated. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the proton conductivity solid electrolyte molding body was obtained. Thus, when the ionic conductivity of the obtained proton conductivity solid electrolyte molding body was measured by the same alternating-current-impedance method as Example 1, the value of 3.2×10^{-3} S/cm was shown. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen but the exterior has flexibility with a higher proton conductivity solid electrolyte molding body by this example. As mentioned above, according to this invention using a proton conductivity inorganic solid electrolyte and a hydrogenation block copolymer, it turned out that it has high processability and a proton conductivity solid electrolyte molding body with high proton conductivity is obtained.

[0055]<<Example 14>> In this example, the silver ion conductivity solid electrolyte molding body was produced using the solid electrolyte expressed with Ag₆I₄WO₄ as a silver ion conductivity solid electrolyte, using (H-1) as a hydrogenation block copolymer. First, Ag₆I₄WO₄ was compounded by the following methods. As a starting material, silver iodide (AgI), silver oxide (Ag₂O), and tungstic oxide (WO₃) were used. These starting materials were mixed, and melting was heated and carried out at 400 ** in the quartz crucible. The silver ion conductivity solid electrolyte which cools radiationally in a furnace after that and is expressed with Ag₆I₄WO₄ was obtained.

[0056]Thus, the obtained silver ion conductivity solid electrolyte was ground, and it stirred in the toluene solution of (H-1). However, it was made for the ratio of the solid electrolyte of silver ion conductivity to the solid content

of a copolymer (H-1) to be set to 97:3 by a weight ratio. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, it dried under decompression of 100 **, and toluene was evaporated. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the silver ion conductivity solid electrolyte molding body was obtained. Thus, the ionic conductivity of the silver ion conductivity solid electrolyte in the obtained silver ion conductivity solid electrolyte molding body and the state where a hydrogenation block copolymer is not added for comparison was measured by the same alternating-current-impedance method as Example 1. As a result, silver ion conductivity solid electrolyte independent ionic conductivity was $4.0 \times 10^{-2} \text{ S/cm}$. On the other hand, in what added the hydrogenation block copolymer, it is $2.3 \times 10^{-2} \text{ S/cm}$ and 1/less than 2 had been the ion-conductive fall rate as compared with the former. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen but the exterior has flexibility with a higher silver ion conductivity solid electrolyte molding body by this example.

[0057]<<Example 15>> The electrode molding body was obtained for the lithium cobalt oxide expressed with LiCoO_2 which is an electronic-lithium ion mixed conductor as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte, using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. First, LiCoO_2 was compounded weighing and by mixing and calcinating at 900 ** among the atmosphere so that it might become a ratio of $\text{Co/Li}=1$ about cobalt oxide (Co_3O_4) and lithium carbonate (Li_2CO_3). Thus, the electrode molding body was obtained by the following method from obtained LiCoO_2 and (H-1). First, LiCoO_2 obtained above was ground to 350 or less meshes. The toluene solution of (H-1) was added to this LiCoO_2 powder, and it fully kneaded, and was considered as slurry form. It was made for the solid content of a hydrogenation block copolymer and the weight ratio of LiCoO_2 powder to be set to 5:95 as for the mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and diameter 10mmphi and a 0.2-mm-thick electrode molding body were obtained by clipping after that. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the water dispersion of poly ethylene tetrafluoride (it expresses with PTFE below.). Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the LiCoO_2 was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0058]Thus, the following alternating-current-impedance method estimated the electrochemical characteristic of the obtained electrode molding body. The outline composition of a measuring device is shown in drawing 1. One expresses a sample electrode holder among a figure. This electrode holder was made to weld the electrode molding body 2 by pressure to the lead terminal 3, and it set to it, and was made it with the examination pole. This examination pole was immersed into the electrolysis solution 4 in the container 7. An electrolysis solution dissolves 6 lithium-fluoride phosphorus (LiPF_6) in the mixed solvent which mixed propylene carbonate and dimethoxyethane at a rate of the volume ratio 1:1 so that it may become the concentration of 1.0M. It was immersed into the electrolysis solution at the reference pole 5 and the counter electrode 6 using the foil of metal lithium, respectively. In this way, it was considered as the measuring cell. With the impedance analyzer, the volts alternating current of 10 mV was impressed to such a measuring cell, and alternating-current-impedance measurement was performed to it in the frequency range (100 kHz – 1 mHz).

[0059]As a result, when the electrode molding body obtained without adding a binder was used, the moldability of the electrode was bad, during measurement, LiCoO_2 which is an electrode active material dropped out in the electrolysis solution, and impedance was not able to be measured. The impedance spectrum acquired about the thing using PTFE which is a hydrogenation block copolymer by this invention and a comparative example as a binder was shown in drawing 2. When the specific polymer by this invention was used as a binder so that more clearly than this figure, it turned out that the electrode molding body which impedance shows a low value and shows the high electrode reaction characteristic is obtained. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0060]<<Example 16>> It replaced with having used in Example 15 as a hydrogenation block copolymer polymer (H-1), and except having used (H-2), it is the same method as Example 15, and the electrode molding body was

obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 310ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0061]<<Example 17>> It replaced with having used in Example 15 as a hydrogenation block copolymer (H-1), and except having used (H-3), it is the same method as Example 15, and the electrode molding body was obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 270ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0062]<<Example 18>> It replaced with having used in Example 15 as a hydrogenation block copolymer (H-1), and except having used (H-4), it is the same method as Example 15, and the electrode molding body was obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 420ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0063]<<Example 19>> Replace with the lithium cobalt oxide expressed with LiCoO_2 used in Example 15 as an electronic-lithium ion mixed conductor, and LiNiO_2 , (H-2) was used for Example 16 and the appearance as a hydrogenation block copolymer, respectively, and the electrode molding body was constituted. The details are shown below. First, lithium hydroxide was mixed with nickel oxide (NiO), and LiNiO_2 was compounded by heating at 800 ** among the atmosphere. Next, LiNiO_2 obtained above was ground to 350 or less meshes. The electrode molding body was obtained by the same method as Example 15 using this LiNiO_2 powder and the toluene solution of (H-2). For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the toluene solution of block copolymer SEBS used by the comparative example 1. Binders, such as a specific polymer, were not added for comparison, but pressing of the LiNiO_2 was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained. Thus, the same alternating-current-impedance method as Example 15 estimated the electrochemical characteristic of the obtained electrode molding body.

[0064]As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, LiNiO_2 which is an electrode active material dropped out in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed the thing using SEBS which are a hydrogenation block copolymer by this invention, and a comparative example as a binder, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 450ohms in 10 mHz, In the electrode molding body using SEBS in a comparative example, it is 740ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0065]<<Example 20>> as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, the lithium manganic acid ghost expressed with LiMn_2O_4 -- as a hydrogenation block copolymer -- Example 16 -- being the same (H-2) -- it used, respectively and the electrode molding body was constituted. The details are shown below. LiMn_2O_4 mixed manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2$) with lithium carbonate (Li_2CO_3), and compounded it by heating at 750 ** among the atmosphere. Next, LiMn_2O_4 obtained above was ground to 350 or less meshes. Graphite powder was mixed with this LiMn_2O_4 powder at a rate of 9:1 by the weight ratio as a electron conductive substance. The electrode molding body was obtained by the same method as Example 15 using the toluene solution [further / (H-2)]. However, it was made for the solid content of a hydrogenation block copolymer and the weight ratio of LiMn_2O_4 powder to be set to 5:95 as for the mixture ratio at the time of kneading. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the water dispersion of PTFE. Binders,

such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiMn_2O_4 powder and black lead was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0066] Thus, the same alternating-current-impedance method as Example 15 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, LiMn_2O_4 which is an electrode active material dropped out in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed the thing using PTFE which is a hydrogenation block copolymer by this invention, and a comparative example as a binder, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 570ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 810ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0067] <<Example 21>> Graphite fluoride was used as a substance in which an electrochemical reduction reaction is shown in the electrolyte which has lithium ion conductivity, (H-2) was used for Example 16 and the appearance as a hydrogenation block copolymer, respectively, and the electrode molding body was constituted. The details are shown below. Graphite fluoride was compounded by heating graphite powder at 600 ** among fluorine gas. Thus, except having replaced the obtained graphite fluoride with LiMn_2O_4 and having used it, the electrode molding body for the electrode molding body by this invention and comparison was formed like Example 20, and the electrochemical characteristics were investigated. As a result, when the electrode obtained without adding a binder was molded, the moldability of the electrode was bad, during measurement, the graphite fluoride which is an electrode active material was omitted in the electrolysis solution, and impedance was not able to be measured. The result of the alternating-current-impedance measurement which followed as a binder the hydrogenation block copolymer by this invention, and the electrode molding body using PTFE which is a comparative example, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 770ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 890ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0068] <<Example 22>> It replaced with LiCoO_2 , and as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, except having used natural graphite, the electrode molding body was constituted like Example 16, and the electrode characteristic was investigated. As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, natural graphite which is an electrode active material was omitted in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed as a binder the hydrogenation block copolymer by this invention, and the electrode molding body using PTFE which is a comparative example, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 370ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 520ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0069] <<Example 23>> LiCoO_2 obtained in Example 15 as an electronic-lithium ion mixed conductor, The electrode molding body was obtained for the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ obtained in Example 5 as a lithium-ion-conductivity inorganic solid electrolyte, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. The electrode molding body was obtained by the following method from the solid electrolyte obtained in Example 5, and LiCoO_2 and the hydrogenation block copolymer (H-2) which were obtained in Example 15. First, the solid electrolyte obtained above was ground to 350 or less meshes. This solid electrolyte powder, LiCoO_2 powder, and the toluene solution of (H-2) were fully kneaded, and it was considered as slurry form. It was made for the weight ratio of the solid content of a hydrogenation block copolymer, solid electrolyte powder, and LiCoO_2 powder to be set to 1:32:67 as for the

mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and diameter 10mmphi and a 0.2-mm-thick electrode molding body were obtained by clipping after that. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the toluene solution of SEBS used by the comparative example 1. Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiCoO_2 and a solid electrolyte was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0070] Thus, the following alternating-current-impedance method estimated the electrochemical characteristic of the obtained electrode molding body. The outline composition of a measuring device is shown in drawing 3. 11 express the hollow sample electrode holder made from polyethylene terephthalate among a figure. The lead terminal 13 was made to weld the electrode molding body 12 by pressure to this electrode holder, and it was considered as the examination pole. This examination pole and the counter electrode 15 which welds metal lithium foil by pressure to the lead terminal 14 were molded into one via the above-mentioned lithium ion conductive solid electrolyte 16, and was used as the measuring cell. With the impedance analyzer, the volts alternating current of 10 mV was impressed to such a measuring cell, and alternating-current-impedance measurement was performed to it in the frequency range (100 kHz - 1 MHz).

[0071] The impedance spectrum acquired as a result was shown in drawing 4. When the hydrogenation block copolymer by this invention is used as a binder so that more clearly than this figure, Although it was high when compared with what did not use a binder, it turned out that the electrode molding body which shows impedance lower than the case where SEBS is used as a binder, and shows the high electrode reaction characteristic is obtained. Next, the drop test estimated the moldability of these electrode molding bodies. From 50 cm in height, the drop test dropped the electrode molding body on the board of marble, and observed the situation of the electrode molding body after fall. As a result, although abnormalities were not looked at by the molding body about the thing using the hydrogenation block copolymer by this invention as a binder, and the thing using SEBS as a binder, the molding body was cracked about what did not use a binder. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0072] <<Example 24>> LiNiO_2 obtained in Example 19 as an electronic-lithium ion mixed conductor, As a lithium-ion-conductivity inorganic solid electrolyte. The noncrystalline solid electrolyte expressed with $0.05\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ which was replaced with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ obtained in Example 5, and was obtained in Example 6, The electrode molding body was obtained using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. The electrode molding body was obtained by the solid electrolyte obtained in Example 6, LiNiO_2 obtained in Example 19, and the method more nearly same than a hydrogenation block copolymer (H-1) as Example 23. Furthermore, for comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was obtained in a similar manner using the toluene solution of SEBS. Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiNiO_2 and a solid electrolyte was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0073] Thus, the same alternating-current-impedance method as Example 23 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the impedance at 10 mHz at the time of using the hydrogenation block copolymer by this invention as a binder was $3.3 \times 10^3 \Omega$. When a binder was not used and SEBS was used as $1.7 \times 10^3 \Omega$ and a binder to it, it was $5.4 \times 10^3 \Omega$. Although the electrode molding body by this example was high when it was compared with what did not use a binder, it turned out that the electrode molding body which shows a value lower than the case where SEBS is used as a binder, and shows the high electrode reaction characteristic is obtained. Next, when the same method as Example 23 estimated the moldability of these electrode molding bodies, abnormalities were not looked at by the molding body about the thing using the hydrogenation block copolymer by this invention as a binder, and the thing using SEBS as a binder, but. The molding body was cracked about what did not use a binder.

[0074] <<Example 25>> It replaces with the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ used in Example 23 as a lithium-ion-conductivity inorganic solid electrolyte, The electrode molding body

was constituted like Example 23 except having used the lithium ion conductive solid electrolyte of the crystalline substance expressed with $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$. The details are shown below. As raw material of a solid electrolyte, lithium carbonate, an aluminum oxide, titanium oxide, and orthophosphoric acid were used. After mixing these starting materials, the lithium-ion-conductivity inorganic solid electrolyte of the crystalline substance which carries out application-of-pressure molding at a pellet type, calcinates at 1300 ** for 24 hours, and is expressed with $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ was obtained. 0. The electrode molding body was obtained by the same method as Example 23 except having replaced with the noncrystalline solid electrolyte expressed with $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, and having used this solid electrolyte. Furthermore, for comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was obtained in a similar manner using the water dispersion of PTFE.

[0075]Thus, the same alternating-current-impedance method as Example 23 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the impedance of the electrode molding body using a hydrogenation block copolymer is $2.8 \times 10^{-3} \Omega$ in 10 mHz.

The impedance of the electrode molding body using PTFE was $4.8 \times 10^{-3} \Omega$. It turned out that the electrode molding body using the hydrogenation block copolymer by this invention as a binder shows lower impedance from the above result. Next, as for no electrode molding bodies using the thing using the hydrogenation block copolymer by this invention as a binder, and PTFE as a binder, the molding body was destroyed when the same method as Example 23 estimated the moldability of these electrode molding bodies. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0076]<<Example 26>> The electrode molding body was further obtained for the lithium cobalt oxide expressed with LiCoO_2 used in Example 15 as an electronic-lithium ion mixed conductor, using a polyethylene mesh as a structure, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. The slurry containing LiCoO_2 and a hydrogenation block copolymer was obtained by the same method as Example 15. Then, the opening of the polyethylene mesh of 70% of a numerical aperture was filled up with this slurry with the doctor blade method. Then, toluene was evaporated under decompression of 120 **, it dried, and the electrode molding body was obtained. When the alternating current impedance of this electrode molding body was measured like Example 15, the almost same impedance as the electrode molding body obtained in Example 15 was shown.

[0077]Next, the bending test was done in order to investigate that flexibility as evaluation of the moldability of this electrode molding body. The bending test twisted this electrode molding body around the stainless steel stick with a diameter [phi] of 40 mm, and viewed the state of the molding body. As a result, as for it, the electrode molding body in this example turned out that abnormalities are not seen but the exterior has high flexibility also by this bending test. The molding body was cracked when the same bending test was done to the electrode molding body obtained in Example 15 to it. As mentioned above, according to the substance and this invention using a structure further which show an electrochemical oxidation-reduction reaction in a hydrogenation block copolymer and the electrolyte which has lithium ion conductivity, it turned out that an electrode molding body with high moldability and the high electrochemical reaction characteristic is obtained especially.

[0078]<<Example 27>> LiNiO_2 which was replaced with LiCoO_2 used in Example 26 as an electronic-lithium ion mixed conductor, and was obtained in Example 19, The electrode molding body consisted of the same methods as Example 26 except having replaced with the polyethylene mesh used in Example 26, and having used the mesh made from stainless steel as a structure of electron conductivity as a structure like Example 26, as a hydrogenation block copolymer, using H-2 respectively. When the alternating current impedance of this electrode molding body is measured like Example 15, it is 390 ohms in value, and impedance lower than the electrode molding body obtained in Example 19 was shown. Next, the bending test was done in order to investigate that flexibility as evaluation of the moldability of this electrode molding body. The bending test twisted this electrode molding body around the Indanthrene loess reinforcing bars of 40 mmphi, and viewed the state of the molding body. As a result, as for it, the electrode molding body in this example turned out that abnormalities are not seen but the exterior has high flexibility also by this bending test.

[0079]<<Example 28>> The electrode molding body obtained in Example 15 as an anode, the electrode molding body obtained in Example 22 as a negative electrode, The lithium cell was obtained using respectively the lithium-ion-conductivity electrolyte which dissolved 6 lithium-fluoride phosphorus (LiPF_6) in the mixed solvent of

propylene carbonate and dimethoxyethane as a lithium ion conductivity electrolyte. The details are shown below. First, the anode molding body and the negative-electrode molding body were obtained by clipping the electrode molding body obtained in the electrode molding body and Example 22 which were acquired in Example 15. The lithium ion conductivity liquid electrolyte dissolved 6 lithium-fluoride phosphorus in the mixed solvent which mixed propylene carbonate and dimethoxyethane at a rate of the volume ratio 1:1 so that it might become the concentration of 1.0M, and it prepared it. The lithium cell with SEBARETA made from porous polyethylene made to intervene between the above-mentioned anode molding body, a negative-electrode molding body, and both and the section shown in drawing 5 using the lithium-ion-conductivity electrolyte was constituted. In drawing 5, 21 expresses the anode molding body arranged in the center of the cell case 24. After allotting the separator 23 and the negative-electrode molding body 22 and dropping the lithium-ion-conductivity electrolyte on this anode molding body 21, the whole was closed with the battery lid 26 via the gasket 25.

[0080]For comparison, it replaced with the anode molding body and negative-electrode molding body which were used by this example, and the lithium cell consisted of Example 15 and Example 22 using an anode molding body and a negative-electrode molding body using PTFE obtained for comparison as a binder. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the lithium cell consisted of following methods, using a solid polymer electrolyte as a binder. As a solid polymer electrolyte, lithium perchlorate (LiClO_4) / polyethylene oxide (PEO) system was used. First, polyethylene oxide (it expresses with the following PEO.) was dissolved in acetonitrile, and LiClO_4 was dissolved further. However, it was made, as for the mixture ratio of PEO and LiClO_4 , for lithium in LiClO_4 to serve as 1/50 of ratios to oxygen in PEO. Thus, the lithium cell consisted of the same methods as the above except having used the obtained solution.

[0081]Thus, the constituted lithium cell was charged to 4.2V with the current value of 1 mA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 1 mA in the voltage range of 3.0V-4.2V. As a result, in the lithium cell using a solid polymer electrolyte, abnormalities were observed in the charging curve during charge of a cell. In order to explore the cause, when the cell was disassembled, no positive and negative poles stopped the shape at the time of battery construction, but the electrode was swelling remarkably, and the current collection nature of the active material was lost. This is considered that the moldability of the electrode was lost when the solid polymer electrolyte dissolved into the electrolyte. Below, service capacity [in / for the internal impedance of the cell obtained by the above-mentioned examination as a binder about the lithium cell using the hydrogenation block copolymer by this invention and the lithium cell using PTFE as a binder / to Table 5 / each charging and discharging cycle] is shown in drawing 6, respectively. Although the fall of the service capacity accompanying a charging and discharging cycle was not observed about which lithium cell, either, it turns out that the direction of the lithium cell using the hydrogenation block copolymer by this invention shows low internal impedance, and serves as a cell also with big service capacity. According to this invention, it turned out that the moldability of an electrode can be improved and the lithium cell in which the outstanding battery characteristic is shown is obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0082]
[Table 5]

電池	内部インピーダンス (Ω)
水素添加ブロック共重合体使用	62
P T F E 使用	102

[0083]<<Example 29>> Except having used the electrode molding body obtained in Example 16 as an electrode molding body used for an anode, it was the same method as Example 28, and the lithium cell by this invention was constituted and the characteristic was evaluated. As a result, the lithium cell which added the hydrogenation block copolymer by this invention, 64-ohm internal impedance was indicated to be the service capacity of 14 or more mAh, and high service capacity and low internal impedance were shown compared with the lithium cell which

used PTFE as a binder and constituted it from Example 28 for comparison.

[0084]<<Example 30>> Except having used the electrode molding body obtained in Example 19 as an electrode molding body used for an anode, it was the same method as Example 28, and the lithium cell by this invention was constituted and the characteristic was evaluated. For comparison, the lithium cell was constituted using the electrode molding body which used SEBS for the binder of the comparative example in Example 19 as an anode, and the characteristic was evaluated. As a result, the service capacity of the lithium cell which added the hydrogenation block copolymer according to this invention is 18mAh.

Internal impedance was 87ohms.

To it, with the lithium cell constituted using SEBS of a comparative example as a binder, service capacity is 16mAh, internal impedance is 98ohms, and the direction of the lithium cell by this invention showed high service capacity and low internal impedance.

[0085]<<Example 31>> The electrode molding body constituted from the same method as Example 15 except having used the titanium disulfide which replaces with the lithium cobalt oxide expressed with LiCoO_2 , and is expressed with TiS_2 as positive active material Anode, It replaced with the natural graphite used in Example 29 as negative electrode active material, and the lithium cell was constituted, using metal lithium respectively. The details are shown below. First, TiS_2 was compounded with the CVD method from titanium metal and sulfur. Next, TiS_2 obtained above was ground to 350 or less meshes. This TiS_2 powder was replaced with LiCoO_2 powder, and was used, and the electrode molding body was obtained by the same method as Example 15. The lithium cell by this invention consisted of the same methods as Example 29 except having used this electrode molding body for the anode, and having used metal lithium foil for the negative electrode, respectively. It replaced with the hydrogenation block copolymer (H-1) for comparison, and the lithium cell using PTFE was also constituted.

[0086]Thus, the constituted lithium cell was discharged to 1.8V with the current value of 500microA. After discharge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 500microA in the voltage range of 1.8V-2.8V. As a result, the lithium cell using the hydrogenation block copolymer by this invention was [28mAh and internal impedance] 74ohms in discharge quantity of electricity. In the thing using PTFE to it, discharge quantity of electricity was 23mAh, and internal impedance was 86ohms. It turned out that the direction of the cell by this invention shows low internal impedance, and serves as a cell also with big service capacity from the above result.

[0087]<<Example 32>> Except having used as an anode the electrode molding body obtained in Example 20, it is the same method as Example 29, and the lithium cell was constituted. For comparison, except having used the electrode molding body using PTFE of the comparative example in Example 16 as a binder as an anode, it was the same method as the above, and the lithium cell was constituted and the characteristic was evaluated. As a result, the lithium cell using the hydrogenation block copolymer by this invention was [11mAh and internal impedance] 230ohms in service capacity. On the other hand, in the thing using PTFE, service capacity was 8.5mAh and internal impedance was 340ohms. It turned out that the direction of the cell by this invention shows low internal impedance, and serves as a cell also with big service capacity from this result.

[0088]<<Example 33>> Except having used the electrolyte which dissolved LiClO_4 in the mixed solvent of propylene carbonate and dimethoxyethane as a lithium ion conductivity electrolyte, it is the same method as Example 29, and the lithium cell by this invention and the lithium cell for comparison were constituted. As a result, the service capacity and internal impedance of the lithium cell using the hydrogenation block copolymer by this invention are 13mAh and 67ohms, respectively.

In the cell using PTFE to it, they were 11mAh and 71ohms, respectively.

[0089]<<Example 34>> The electrode molding body using the mesh made from stainless steel obtained in Example 27 in order to improve the moldability of an electrode further as an anode is used, Except having used the negative-electrode molding body using the mesh made from stainless steel furthermore indicated below, it is the same method as Example 28, and the lithium cell was constituted. The negative-electrode molding body was obtained by filling up the mesh made from stainless steel with the natural graphite obtained in Example 22, and the slurry containing (H-2), evaporating toluene under decompression of 100 **, and drying. Thus, the lithium cell consisted of the same methods as Example 28, using the obtained negative-electrode molding body and the electrode molding body obtained in Example 27 as an anode. Thus, the place which estimated the characteristic of

the constituted lithium cell as Example 28 similarly, The service capacity of the lithium cell using the structure which the fall of the service capacity accompanying a charging and discharging cycle was not observed, but was further obtained by this example 17mAh, Internal impedance is 51ohms and it turned out that the direction of the cell obtained in this example shows low internal impedance, and serves as a cell also with big service capacity.

[0090]<<Example 35>> In Example 28 – Example 34, although the example which constituted the lithium cell as an electrochemical element was explained, the example which constituted the nickel-cadmium battery as an electrochemical element in this example is explained. First, the electrode molding body used as a negative electrode was produced by the following method. As cadmium oxide powder and a hydrogenation block copolymer, the toluene solution of (H-2) was mixed so that cadmium oxide and a copolymer might be set to 95:5 by a weight ratio. Thus, the electrode molding body was obtained by being applied and filled up with the adjusted slurry at the iron punching metals which performed the nickel plate as a structure of electron conductivity, and evaporating toluene at 100 **. Next, the electrode molding body used as an anode consisted of following methods. Nickel hydroxide, metal cobalt powder, and the toluene solution of (H-2) were mixed so that 90:5:5 might become comparatively by the weight ratio of nickel hydroxide, metal cobalt, and a copolymer. Thus, the electrode molding body was obtained by filling up nickel foam with the adjusted slurry as a structure of electron conductivity, and evaporating toluene at 100 **. Thus, using the obtained anode and the negative electrode, further, the polyamide fiber nonwoven fabric was used as a separator, the KOH solution of 7N was used as an electrolyte, and the nickel-cadmium battery was constituted. Thus, when the charge-and-discharge performance and the rate characteristic of a nickel-cadmium battery which were constituted are investigated, compared with the conventional thing, it is equal. As mentioned above, the hydrogenation block copolymer was understood that it can apply also as a binder used for the electrochemical element which used the quality of aqueous electrolysis.

[0091]<<Example 36>> the lithium cobalt oxide expressed with LiCoO_2 considering (H-1) as positive active material as a hydrogenation block copolymer, All the solid lithium cells were obtained as negative electrode active material, using respectively the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ considering indium as a lithium ion conductivity electrolyte. The details are shown below. What obtained the lithium ion conductive solid electrolyte in Example 5, and LiCoO_2 used what was obtained in Example 15. As a solid electrolyte molding body, what was obtained in Example 5, and the thing obtained in Example 23 as an electrode molding body were used. All the solid lithium cells consisted of these lithium ion conductive solid electrolytes, LiCoO_2 , a solid electrolyte molding body, and an electrode molding body by the following method.

[0092]First, the solid electrolyte layer and the positive electrode layer were produced by the powder molding method, respectively from the lithium ion conductive solid electrolyte which does not contain a hydrogenation block copolymer for comparison, and the positive electrode material, and all the solid lithium cell A with the section shown in drawing 7 was constituted. In drawing 7, the solid electrolyte layer of lithium ion conductivity [31 / 33 / an anode and] and 32 are the metal indium foil of a negative electrode, and application-of-pressure molding of these is carried out at one. The pellet molded into this one was put into the cell case 34 made from stainless steel, and it sealed with the lid 36 made from stainless steel via the insulating gasket 35. Next, it replaced with the above-mentioned lithium ion conductive solid electrolyte powder, and lithium cell B by this invention consisted of the same methods as the above except having used the lithium ion conductive solid electrolyte molded body obtained in Example 5. It replaced with the anode used by the above-mentioned lithium cell A, and lithium cell C by this invention consisted of the same methods as lithium cell A except having used the electrode molding body obtained in Example 23. It replaced with the lithium ion conductive solid electrolyte powder and positive electrode material which were used by lithium cell A, and lithium cell D by this invention consisted of the same methods as lithium cell A except having used the lithium ion conductive solid electrolyte molded body and the electrode molding body, respectively. It replaces with the hydrogenation block copolymer used by this example for comparison below, Using the electrode molding body obtained using the isoprene styrene random copolymer by the same method as the solid electrolyte molding body and/or Example 23 which were acquired by the same method as Example 5, similarly Lithium cell E (a solid electrolyte layer is a solid electrolyte molding body), Lithium cell F (a positive electrode layer is an electrode molding body) and lithium cell G (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were constituted. Thus, the constituted lithium cell was charged to 3.7V with the current value of 300microA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and

discharge test was done with the current value of 300microA in the voltage range of 2.0V-3.8V.

[0093]Service capacity [in / for the internal impedance of the cell obtained as a result / to Table 6 / each charging and discharging cycle] is shown in drawing 8, respectively. In lithium cell B by this invention, C, and D, although internal impedance was high compared with lithium cell A, most falls of the service capacity accompanying a charging and discharging cycle were not observed. In lithium cell A which did not add a hydrogenation block copolymer to it, the fall of the capacity accompanying a charging and discharging cycle was remarkable. In order to explore the cause, when the section is observed by X-ray CT, a crack is observed by the pellet inside a cell and it is thought by the volume change of the electrode accompanying charge and discharge that capacity lowering is carried out because the jointing condition inside a cell got worse. Lithium cell E using the isoprene styrene random copolymer as a binder of a solid electrolyte layer and/or an electrode molding body, F, and G showed the value with high internal impedance after charge, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things. This is considered that the internal impedance of the cell increased, the excess voltage at the time of charge and discharge became big as a result further, and it became what has small service capacity as a result of the added polymer checking the ion conductivity inside a cell. According to this invention, it turned out that the fall of the junction nature inside the cell by the volume change of the electrode at the time of charge and discharge is prevented, and all the solid lithium cells excellent in the charge-discharge cycle characteristic are obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0094]
[Table 6]

	内部インピーダンス (Ω)
電池 A	340
電池 B	470
電池 C	610
電池 D	740
電池 E	2500
電池 F	3100
電池 G	3800

[0095]<<Example 37>> The electrode molding body which was replaced with the electrode molding body used in Example 36 as an anode, and was obtained in Example 24, It is the same method as Example 36 except having used the solid electrolyte molding body which was replaced with the solid electrolyte molding body used in Example 36, and was obtained in Example 6 as a solid electrolyte layer, respectively, All the solid lithium cell I (a solid electrolyte layer is a solid electrolyte molding body) by this invention, lithium cell J (a positive electrode layer is an electrode molding body), and lithium cell K (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were produced, and those characteristics were evaluated. The solid electrolyte layer and the positive electrode layer constituted all the solid lithium cell H which produced the electrolyte and the positive electrode material only by the powder molding method, respectively not using the hydrogenation block copolymer. A comparative example [in / as an electrode molding body / for comparison / Example 24], the electrode molding body using SEBS as a binder, and SEBS -- 3.5wt% -- using the included solid electrolyte molding body, All the solid lithium cell L (a solid electrolyte layer is a solid electrolyte molding body), lithium cell M (a positive electrode layer is an electrode molding body), and lithium cell N (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were constituted.

[0096]As a result, by lithium cell I by this invention, J, and K, as shown in Table 7, although internal impedance was high compared with lithium cell H, most falls of the service capacity accompanying a charging and discharging cycle were not observed. In lithium cell H which did not add a hydrogenation block copolymer to it, the fall of the

capacity accompanying a charging and discharging cycle was remarkable. In order to explore the cause, when the section is observed by X-ray CT, a crack is observed by the pellet inside a cell and it is thought by the volume change of the electrode accompanying charge and discharge that capacity lowering is carried out because the jointing condition inside a cell got worse. Lithium cell L using SEBS, M, and N showed the value with high internal impedance after charge, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things. This is considered that the internal impedance of the cell increased, the excess voltage at the time of charge and discharge became big as a result further, and it became what has small service capacity as a result of the added polymer checking the ion conductivity inside a cell.

[0097]
[Table 7]

	内部インピーダンス (Ω)
電池 H	430
電池 I	570
電池 J	690
電池 K	800
電池 L	2800
電池 M	3300
電池 N	3900

[0098]<<Example 38>> the titanium disulfide expressed with TiS_2 which was replaced with the lithium cobalt oxide expressed with LiCoO_2 used in Example 36 as positive active material, and was obtained in Example 31, It replaced with the indium used in Example 36 as negative electrode active material, and all the solid lithium cells were constituted for metal lithium, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. First, TiS_2 obtained in Example 31 was ground to 350 or less meshes. The electrode molding body was produced by the same method as Example 23 except having replaced this TiS_2 powder with LiCoO_2 powder, and having used it. And the lithium cell by this invention was constituted using this electrode molding body and metal lithium foil. It replaced with the lithium cell and hydrogenation block copolymer which do not add a hydrogenation block copolymer for comparison, and the lithium cell using SEBS was also constituted. Thus, the constituted lithium cell was discharged to 1.8V with the current value of 100microA. After discharge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 100microA in the voltage range of 1.8V-2.8V.

[0099]As a result, the lithium cell which added the hydrogenation block copolymer to either a solid electrolyte layer or a positive electrode layer by this invention is a value below 1komega of what shows slightly high internal impedance compared with what did not add a hydrogenation block copolymer. Most falls of the service capacity accompanying a charging and discharging cycle were not observed. As for the lithium cell using SEBS as a binder, the internal impedance after charge showed the high value more than 2komega. The fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things.

[0100]<<Example 39>> like Example 36 except having used as an anode the electrode molding body using the lithium manganic acid ghost expressed with LiMn_2O_4 which was replaced with the lithium cobalt oxide expressed with LiCoO_2 used in Example 36, and was obtained in Example 20, All the solid lithium cells were constituted. The details are shown below. First, LiMn_2O_4 obtained in Example 20 was ground to 350 or less meshes. This LiMn_2O_4 powder, the solid electrolyte powder obtained in Example 5, and the graphite powder as a electron conductive substance were mixed at a rate of 6:3:1 by the weight ratio, and the positive electrode material was obtained.

Thus, except having used the obtained positive electrode material, the electrode molding body was constituted from the same method as Example 23, and the lithium cell was constituted using this electrode molding body. For comparison, the lithium cell was constituted without adding a hydrogenation block copolymer, it replaced with the hydrogenation block copolymer further, the lithium cell was constituted using SEBS, and those characteristics were evaluated.

[0101]As a result, although the lithium cell which added the hydrogenation block copolymer to either a solid electrolyte layer or a positive electrode layer by this invention shows slightly high internal impedance compared with the lithium cell which did not add a hydrogenation block copolymer, the value is below 1komega. Most falls of the service capacity accompanying a charging and discharging cycle were not observed. As for the lithium cell using SEBS, the internal impedance after charge showed the high value more than 2komega, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things.

[0102]<<Example 40>> Except having replaced with the indium used in Example 36, and having used the electrode molding body using natural graphite as negative electrode active material, it is the same method as Example 36, and all the solid lithium cells by this invention were constituted. The details are shown below. As a negative pole material, what mixed with natural graphite the lithium ion conductive solid electrolyte obtained in Example 36 at a rate of 9:1 by the weight ratio was used. The electrode molding body was obtained by the same method as Example 23 using this negative pole material. Thus, the lithium cell consisted of the same methods as Example 36 using the lithium ion conductive solid electrolyte molded body obtained in the obtained negative-electrode molding body, the anode molding body obtained in Example 23, and Example 5. The lithium cell was constituted without adding a hydrogenation block copolymer for comparison. Thus, the constituted lithium cell was charged to 4.2V with the current value of 300microA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 300microA in the voltage range of 2.5V-4.2V. As a result, although the lithium cell which added the hydrogenation block copolymer by this invention shows slightly high internal impedance compared with the lithium cell which did not add a hydrogenation block copolymer, the value is below 1komega. Most falls of the service capacity accompanying a charging and discharging cycle were not observed.

[0103]<<Example 41>> In order to improve the moldability of an anode further as positive active material, negative electrode active material, and an electrolyte using the same thing as lithium cell C in Example 36, the lithium cell was constituted using the mesh made from stainless steel. First, LiCoO_2 used in Example 36, $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - 0.36SiS_2 , and the slurry containing (H-2) were prepared as positive active material, a solid electrolyte, and a hydrogenation block copolymer. With the doctor blade method, the opening of the mesh made from stainless steel of 80% of the numerical aperture which is a structure was filled up with this slurry. Then, under decompression of 100 **, toluene was evaporated and it dried. Then, it pierced to the discoid of 16 mmphi and the anode molding body was obtained. Thus, the lithium cell consisted of the same methods as lithium cell C in Example 36 using the obtained anode molding body. Thus, the place which estimated the characteristic of the constituted lithium cell as Example 36 similarly, The fall of the service capacity accompanying a charging and discharging cycle was not observed, but the internal impedance of the lithium cell using the structure further obtained by this example is 480ohms, and showed low internal impedance compared with lithium cell C using an anode molding body similarly in Example 36. Service capacity is also 14mAh and it turned out that it is a big thing compared with lithium cell C. According to this invention, by improving the moldability of an electrode and putting a structure in an electrode further showed that the lithium cell in which the more outstanding battery characteristic is shown was obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0104]<<Example 42>> This example explains the example which constituted the electrochromic display device as all the solid electrochemical elements using the proton conductivity solid electrolyte obtained in Example 13. The tungstic oxide (WO_3) thin film was used for the display pole of the electrochromic display device. As shown in drawing 9, the tungstic oxide thin film 43 was formed with electron beam evaporation method on the glass substrate 41 which formed the ITO layer 42 in the surface with weld slag vacuum deposition as a transparent electrode. The tungstic oxide (H_xWO_3) thin film which doped the proton obtained by the following methods was

used for the counter electrode. First, the tungstic oxide thin film was formed on the glass substrate 45 which formed ITO electrode 46 like the above-mentioned display pole. Tungstic oxide was made into tungsten PURONZU (H_xWO_3) 47 by immersing this glass substrate into chloroplatinic acid (H_2PtCl_6) solution, and drying it in a hydrogen air current. The electrolyte layer of the electrochromic display device was formed by the following methods. First, the toluene solution of (H-1) was added to the silica gel which doped the phosphoric acid obtained in Example 13. This electrolyte layer added alumina powder at a rate of 5% by the weight ratio to silica gel, in order to make it color white, since it serves also as the light reflector of an electrochromic display device. This mixture was kneaded until it became slurry form, and it applied to a thickness of 50 micrometers on the surface of the display pole previously obtained with the doctor blade method, and was considered as the electrolyte layer.

[0105] Thus, on the display pole in which the obtained electrolyte layer was formed on the surface, the counter electrode obtained previously was put so that an electrolyte layer might be covered, and to it, the solvent was further volatilized under decompression. The sectional view is shown in drawing 10. Adhesion closure of the end face was carried out with the ultraviolet curing resin 50, and the electrochromic display device was obtained. As for 44, in drawing 10, a counter electrode and 49 are electrolyte layers a display pole and 48, and 51 and 52 are lead terminals. Thus, the voltage of $-1V$ was impressed to the display pole for 2 seconds to the counter electrode, the display pole was colored the obtained electrochromic display device, and the operation cycle test which impresses the voltage of $+1V$ for 2 seconds, and decolorizes it after that was done. As a result, after 10000 cycle progress does not have the fall of performance, and coloring and decolorization were able to be performed. According to this invention, it turned out that the electrochromic display device excellent in the operation cycle characteristic is obtained as mentioned above.

[0106] In the above example, as a lithium-ion-conductivity inorganic solid electrolyte, $0.6Li_2S-0.4SiS_2$, $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$, $0.5Li_2S-0.5P_2S_5$, $0.6Li_2S-0.4B_2S_3$, etc. gave lithium-ion-conductivity noncrystalline solid electrolyte ***** explanation. However, the thing containing other sulfides which were not explained in the examples, such as that from which each ingredient ratio of these solid electrolytes differed, and Li_2S-GeS_2 , The thing containing other lithium halides, such as $LiCl-Li_2S-SiS_2$ and $LiBr-Li_2S-P_2S_5$, $LiI-Li_2S-SiS_2-P_2S_5$, The thing of pseudo-4 element systems, such as $LiI-Li_3PO_4-Li_2S-SiS_2$, etc., Or Li_3N and $Li_{1.3}Sc_{0.3}Ti_{1.7}(PO_4)_3$. It cannot be overemphasized that the same effect is acquired even if it uses the lithium-ion-conductivity inorganic solid electrolyte of other crystalline substances which were not explained in the examples, such as $Li_{0.2}La_{0.6}TiO_3$, either. This invention is not limited to what was explained in these examples as a lithium ion conductive solid electrolyte. Although a lithium cobalt oxide, a lithium nickel oxide, a lithium manganic acid ghost, or graphite fluoride was explained as a substance in which an electrochemical oxidation-reduction reaction is shown in the above example in the electrolyte which has lithium ion conductivity, In addition, it cannot be overemphasized that the same effect is acquired even if it uses the substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has other lithium ion conductivity which was not explained in the example of copper oxide or an iron sulfide, either. As a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, this invention is not limited to what was explained in these examples.

[0107] Although the lithium cell using the electrolyte which dissolved $LiPF_6$ or $LiClO_4$ in the mixed solvent of propylene carbonate and dimethoxyethane was explained as a lithium ion conductivity electrolyte in the example, In addition, the thing using the supporting electrolyte which was not explained in the examples, such as $LiBF_4$, Or in the examples, such as ethylene carbonate, it is not limited to the lithium cell using what it could not be overemphasized that the same effect was acquired also when the electrolyte using the solvent which was not explained is used, either, and explained this invention in these examples as an electrolyte. In an example, although only the thing using a polyethylene mesh and a glass fiber mesh as an electronic insulation structure was explained, It cannot be overemphasized mesh, such as other construction material, for example, polypropylene, polyester, and cellulose, and that the same effect is acquired even if it uses not mesh but these nonwoven fabrics further, either, and this invention as an electronic insulation structure, It is not limited to a polyethylene mesh and a glass fiber mesh. In an example, although only the thing using a stainless steel mesh as a structure of electron conductivity was explained, This invention is not limited to what it could not be overemphasized mesh, such as other construction material, for example, titanium etc., and that the same effect was acquired even if it uses not

mesh but these nonwoven fabrics further, either, and was explained in these examples as a structure.

[0108]

[Effect of the Invention]As mentioned above, according to this invention, the solid electrolyte molding body which combines high ion conductivity and high processability, or an electrode molding body with high electrode activity can be obtained, and the electrochemical element which shows the operational characteristic excellent in using these solid electrolyte molding body and an electrode molding body further can be obtained.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]This invention relates to an electrochemical element, the solid electrolyte molding body used for this electrochemical element, and an electrode molding body. It is adding a high molecular compound in more detail to the electrolyte material which constitutes an electrochemical element, and an electrode material, and is related with the electrochemical element constituted using the molding body holding these electrochemical element component, and these molding bodies.

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PRIOR ART

[Description of the Prior Art]Electrochemical elements including a cell comprise an electrolyte layer which movement of ion produces, and an electrode layer in which transfer of the electron to ion is performed with movement of ion. A high molecular compound is added for the following purpose to these electrolyte layers and an electrode layer.

[0003][Addition to an electrolyte layer] Generally an electrolyte is the fluid in which the solvent was made to dissolve a supporting electrolyte. Since the container which stores this fluid is needed, it is difficult to miniaturize and slim down an electrochemical element.

In order to solve this technical problem, research of all the solid electrochemical elements which replaced with the conventional liquid electrolyte and used the solid electrolyte is done. Especially as an electrochemical element, a lithium cell, Small [the atomic weight of lithium], since ionization energy is a big substance, research is briskly done as a cell which can obtain high energy density, and it has come to be broadly used as a power supply of a portable device now. A close-up of the concern about the safety of a cell has been taken by the increase in the internal energy according to the increase in the amount of content active materials along with wide use of a lithium cell on the other hand, and the increase in the content of the organic solvent which is the combustible material further used for the electrolyte in recent years.

[0004]It is very effective to replace with an organic solvent electrolyte and to use the solid electrolyte which is a noncombustible substance as a method for securing the safety of a lithium cell. Therefore, also in order to secure high safety in addition to above-mentioned miniaturization and slimming down, it is important for a lithium cell to use a solid electrolyte. As a lithium ion conductivity solid electrolyte used for such a cell, lithium halide, lithium nitride, and lithium acid matter acid chloride or these derivatives are known. $\text{Li}_2\text{S}-\text{SiS}_2$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, Lithium-ion-conductivity sulfide noncrystalline solid electrolytes, such as $\text{Li}_2\text{S}-\text{B}_2\text{S}_3$, It is known that the lithium ion conductive solid electrolyte which doped lithium salt, such as lithium halides, such as LiI , or Li_3PO_4 , on these glass shows the high ion conductivity more than $10^{-4} - 10^{-3}\text{S/cm}$. The solid polymer electrolyte which consists of organic matters is obtained by evaporating a solvent from the solution of lithium salt and an organic polymer compound to the solid electrolyte of these inorganic matter. Compared with an inorganic solid electrolyte, thin-film-izing is easy for this solid polymer electrolyte, and the solid electrolyte thin film obtained is also rich in processability, such as having flexibility.

[0005]In recent years as a solid electrolyte which has flexibility or rubber elasticity, the proposal of the new solid electrolyte named the "polymer in salt" type which consists of mineral salt which has very high-concentration lithium ion conductivity compared with the above-mentioned solid polymer electrolyte, and polymers is proposed (C. -- A. --) [Angell and] C. Liu, and E. Sanchez, Nature, and vol.632 (1993), 137. Also in the electrochemical element using a liquid electrolyte, the porous high molecular compound is usually used for the electrolyte layer as a separator. In [excel in the water addition nature which holds a liquid electrolyte while preventing inter-electrode electronic contact mechanically, and] an electrochemical element, a separator needs to be chemically stable, and a also electrochemically stable thing is required from being used where an electrode is contacted further.

[0006][Addition to an electrode layer] An electrode comprises molding an electrode active material and making a charge collector contact. When an electrode active material is only molded by the application-of-pressure molding method, the cohesive force between electrode active material particles is mainly only Van der Waals force. However, since the usual electrochemical element uses the fluid as an electrolyte, when the electrode

molding body constituted only by the application-of-pressure molding method in this way is immersed into a liquid electrolyte. The cohesive force between active material particles declines, and from an electrode molding body, an electrode active material particle drops out in a liquid electrolyte, and cannot hold shape of an electrode molding body because liquid molecules stick to an electrode active material particle surface. Therefore, in order to improve the moldability of an electrode, a high molecular compound is generally added to an electrode molding body as a binder.

[0007]To the electrolyte layer or electrode layer of an electrochemical element, although a high molecular compound is added for the above-mentioned purpose, these Prior arts have the following problem. The above-mentioned inorganic solid electrolyte is ceramics or glass.

When applying to a cell generally, it is used as a pellet which carried out application-of-pressure molding of the ground solid electrolyte powder.

However, since [with it] the pellet obtained was weak, it had the problem that it was lacking in processability and slimming down was difficult. [hard] The ionic conductivity of below 10^{-4} S/cm is [the solid electrolyte which consists of organic matters on the other hand] low at a room temperature.

As an electrolyte for lithium cells of practical use, it was insufficient. In order to solve this problem, the proposal of the solid polymer electrolyte which improved ion conductivity is also made by adding a plasticizer. However, a plasticizer is a thing of an original inflammability and the problem of the transference number of a lithium ion falling or reactivity with a lithium anode falling generates it conversely by adding a plasticizer. and addition of a plasticizer -- it is hard to say what has performance with a solid electrolyte of these organicity sufficient as an electrolyte for lithium cells irrespective of how.

[0008]Below 10^{-4} S/cm has [the conductivity of an above-mentioned "polymer in salt" type solid electrolyte] low most.

What has ionic conductivity sufficient as an electrolyte for lithium cells cannot say. Although high ion conductivity was shown when room temperature fused salt, such as $\text{AlCl}_3\text{-LiBr-LiClO}_4$, was used as mineral salt, it was easy to produce reduction of electrochemical aluminum, and it was not able to be said that it was suitable as an electrolyte for lithium cells.

[0009]As stated previously, an electrode molding body comprises a mixture which mixed the high molecular compound as a binder to the electrode active material. A high molecular compound is generally a thing of electric insulation.

It is easy to check movement of ion and the ionic diffusion in the electrochemical reaction produced in an electrode/electrolyte interface and also an electrode is checked. And in order to improve moldability, when the mixture ratio of a high molecular compound was raised, it had the problem that the operational characteristic of an electrochemical element fell easily. An electrode molding body fills up with or applies to a charge collector the slurry which mixed the mixture of the electron conductive substance added if needed in carrier fluid in order to improve the electron conductivity in an electrode active material, a binder, and an electrode, and is constituted by evaporating carrier fluid. As for the high molecular compound used as a binder, in order to improve the coating nature of a slurry, and restoration nature, it is preferred that it is a thing of fusibility to the carrier fluid to be used.

[0010]When a solid electrolyte is used as an electrolyte, omission into the electrolyte of an electrode active material particle are prevented. However, in order to use an electrode molding body as an electrode active material and to only make reaction surface area into a big thing also in that case, when it is considered as the application-of-pressure molding body of the mixture which mixed the electrode active material and the solid electrolyte. The electrode molding body had the problem that it became hard weak processability with a scarce thing, and the composition of an electrochemical element will become difficult. Since a contact interface with an electrode active material turns into an interface of a solid/solid when a solid electrolyte is used as an electrolyte, compared with the case where a liquid electrolyte is used, it becomes what has a small touch area of an electrode active material and an electrolyte. Therefore, the tendency used as a big thing has electrode reaction resistance. In order to improve moldability, the tendency becomes still more remarkable when the high molecular compound of electric insulation is added. Therefore, it had the problem that an electrode reaction rate fell easily. If a lithium cell is mentioned as an example of an electrochemical element, as an electrode active material, a lithium cobalt oxide (Li_xCoO_2) will be used for an anode, and black lead etc. will be used for a negative electrode, respectively. When it used for the lithium cell as an electrode molding body by which application-of-pressure

molding was carried out as stated also in advance since these were obtained as powder, the electrolyte of the fluid invaded among electrode configuration particles, the electrode swelled, and maintaining shape had the problem that electric contact was also easy to be lost difficult. Li_xCoO_2 has the structure in which the triangular lattice of oxygen, lithium, and cobalt was piled up in order of O-Li-O-Co-O-Li-O .

A lithium ion exists between the layers of CoO_2 .

A lithium ion goes in and out between CoO_2 layers by the electrochemical oxidation-reduction reaction in the inside of a lithium ion conductivity electrolyte. As a result, the size of the electric interaction between CoO_2 layers changes, elasticity arises between layers, and a volume change arises in an electrode. Therefore, whenever it repeated charge and discharge, the junction between the particles which constitute an electrode was easy to be lost, and it had a problem of capacity falling in connection with a charging and discharging cycle.

[0011]As mentioned above, although Li_xCoO_2 was explained as an electrode active material, As an active material in which application of the substance conventionally used as an active material for lithium cells or future is expected, Transition metal bisulfides, such as transition metal oxides, such as Li_xNiO_2 , Li_xMnO_2 , and MnO_2 , and Li_xTiS_2 , or a graphite lamellar compound, graphite fluoride, etc. are mentioned. Also when such materials are used, the same problem arises. When a solid electrolyte is used as an electrolyte, it is in the tendency which becomes what has a small touch area between a solid electrolyte and an electrode active material as stated also in advance. Therefore, when the volume change of the electrode active material accompanying the charge and discharge of a cell arises, junction between an active material and an electrolyte is easier to be lost. Since the elastic body which absorbs the volume change of an electrode active material in the case of charge and discharge does not exist in the inside of a cell as a result of all the battery materials' comprising a hard solid, there is a possibility that change of battery size and poor obturation of the cell obturation part accompanying this may arise.

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EFFECT OF THE INVENTION

[Effect of the Invention]As mentioned above, according to this invention, the solid electrolyte molding body which combines high ion conductivity and high processability, or an electrode molding body with high electrode activity can be obtained, and the electrochemical element which shows the operational characteristic excellent in using these solid electrolyte molding body and an electrode molding body further can be obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the solid electrolyte molding body which solves the above technical problem, shows outstanding electrochemical characteristics including high ion conductivity, has flexibility further, and was excellent in processability. Another purpose of this invention is to provide the electrode molding body which could constitute the electrochemical element which shows the outstanding operational characteristic, and was excellent in moldability and processability. The further purpose of this invention is to provide the electrochemical element which solves the technical problem resulting from the volume change of the electrode active material under operation of these electrochemical elements, and stabilizes and operates.

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MEANS

[Means for Solving the Problem]A block with which a solid electrolyte molding body of this invention consists of polybutadiene whose (A)1,2-vinyl bond content is 15% or less, (B) It consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, And a 1,2-vinyl bond content of a butadiene part consists of a block which consists of a butadiene (**) polymer which is 20 to 90%, And it consists of a hydrogenation block copolymer produced by hydrogenating a straight chain or a branched state block copolymer which is (A)/(B) = 5 - 70 / 95 to 30 % of the weight, and a solid electrolyte. An electrode molding body of this invention comprises an electrode active material and an aforementioned hydrogenation block copolymer. An electrochemical element of this invention possesses an electrode and an electrolyte layer of a couple, and considers at least one of an electrode of said couple, and the electrolyte layers as composition containing the above-mentioned hydrogenation block copolymer.

[0014]A hydrogenation block copolymer which is one of the main ingredients of this invention, A polybutadiene block (A) whose 1 and 2-vinyl bond content is 15% or less. It consists (it is hereafter called the block A) of at least one piece, 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, And a butadiene (**) polymer whose 1,2-joint content of a butadiene part is 20 to 90%. A straight chain whose rates of the block A in a molecule and the block B it has at least one (it being hereafter called the block B), and are 5-70/95-30 (% of the weight), or a branched state block polymer. It is a hydrogenation block polymer produced by carrying out hydrogenation of (calling it a non-hydrogenated block polymer hereafter) not less than 90%. The block A turns into crystalline polyethylene similar structure blocks by hydrogenation, and the block B of a hydrogenation block polymer turns into a rubber-like block of an olefin skeleton.

[0015]Here, a lithium ion conductive solid electrolyte is used as a solid electrolyte of a solid electrolyte molding body. A noncrystalline solid electrolyte is used as a solid electrolyte. As a lithium ion noncrystalline solid electrolyte, a thing which makes a sulfide a subject, especially a thing containing silicon are used suitably. The solid electrolyte molding body can contain a structure of electronic insulation.

[0016]As for an electrode molding body, it is preferred that a lithium-ion-conductivity inorganic solid electrolyte is included. As a lithium-ion-conductivity inorganic solid electrolyte, an amorphous thing which made a sulfide a subject is used suitably. As for an electrode molding body, it is preferred that a structure is included, and thing of a structure of electron conductivity is more preferred.

[0017]

[Embodiment of the Invention]This invention persons by using the hydrogenation block copolymer which has crystalline polyethylene similar structure blocks and the rubber-like block of an olefin skeleton as a high molecular compound, Movement of the ion between the substances which constitute electrochemical elements, such as an electrode active material / electrolyte interface, is made easy between inorganic solid electrolyte particles and between electrode active material particles, high moldability and flexibility are given to a solid electrolyte molding body, an electrode molding body, etc., and it is based on having found out that processability could be improved. For example, if a high molecular compound is mixed in order to give flexibility to an inorganic solid electrolyte, the surface of inorganic solid electrolyte particles will be in the state where it was covered with the insulating high molecular compound. As a result, the ion conduction between solid electrolyte particles is checked, and the ionic conductivity of the complex of the ion-conductive inorganic solid electrolyte obtained and a high molecular compound will become low. By however, the thing for which the hydrogenation block polymer which has the crystalline polyethylene similar structure blocks and the rubber-like block of an olefin skeleton by this invention is used as a high molecular compound. Without spoiling high ion conductivity greatly, the binding property between solid electrolyte particles can be improved, and flexibility etc. can be given to the molding body

of a solid electrolyte. By introducing crystalline polyethylene similar structure blocks, the hydrogenation block copolymer of this invention is that a little addition can also give flexibility, and can obtain the lithium-ion-conductivity molding body which has high conductivity.

[0018]It explains to details per this invention below. The 1,2-vinyl bond content of the block A before hydrogenation is an important factor which determines the cohesive force of the melting point resulting from the block A, and polyethylene similar structure blocks after hydrogenation. If especially cohesive force declines, it becomes impossible to lessen an addition and a high lithium-ion-conductivity complex cannot be obtained. 1 of the block A and 2-vinyl bond content need to be 15% or less. If 1 of the block A and the amount of 2-vinyl bonds exceed 15%, the cohesive force of the block A after hydrogenation declines, and it is not desirable, and since the melting point also falls, heat resistance also falls and it is not desirable. The block B before hydrogenation consists of 50 to 100 % of the weight of butadiene, and 0 to 50 % of the weight of other monomers, and the 1,2-vinyl bond content of a butadiene part is a block segment which consists of a butadiene (**) polymer which is 20 to 90%, and it turns into a block like rubber by hydrogenation. In the block B, since 1 of a butadiene part and 2-vinyl bond content serve as butene structure by hydrogenation, the content has direct influence on the glass transition temperature resulting from the block B after hydrogenation, and serves as a factor which influences flexibility in a complex with a lithium ion conductive solid electrolyte.

[0019]In this invention, 1 of the block B and 2-vinyl bond content need to be not less than 20% and 90% or less. It is not desirable, in order that an after-hydrogenation crystallinity portion may arise and 1 of the block B and 2-vinyl bond content may reduce flexibility in less than 20%. If 90% is exceeded, in order for a butene content to increase too much and to raise glass transition temperature, since flexibility is reduced, it is not desirable. As butadiene in the block B, and other copolymerizable monomers, although acrylic ester (meta), such as aromatic vinyl compounds, such as styrene, alpha-methylstyrene, and ****- methylstyrene, methyl methacrylate, and methyl acrylate, isoprene, etc. are mentioned, Especially styrene and isoprene are preferred. The amount of these monomers used is 0 to 50% of total monomers which constitute the block B. If 50% is exceeded when using other monomers, since the flexibility after hydrogenation falls, it is not desirable. In the block copolymer before hydrogenation, it may have a polymeric block (henceforth the block X) which is mainly concerned with an aromatic vinyl compound.

[0020]The hydrogenation block copolymer of this invention is a hydrogenation block copolymer produced by hydrogenating at least one block A, at least one block B, the straight chain that has the block X if needed further, or a branched state block copolymer. a non-hydrogenation block copolymer -- concrete -- $A-(B-A)_l$ and $m(A-B)$ (1 or more [However, l and m]) -- or $(A-B-X)_n$ (1 or more [However, n]) -- it is shown by the structural formula. In the block copolymer which has such a structure, an A-B-A type triblock copolymer and the triblock copolymer of an A-B-X (X is polystyrene block) mold are preferred.

[0021]The ratios of the block A and the block B occupied in a non-hydrogenation block copolymer are block A / block B= 5-70 / 95 to 30 % of the weight. Since crystalline block segments run short when the block B exceeds 95 % of the weight at less than 5 % of the weight in the block A of a non-hydrogenation block copolymer, cohesive force cannot decline and high moldability cannot be obtained in the range with few additions to a solid electrolyte. When the block A is [the block B] less than 30 % of the weight exceeding 70 % of the weight, the hardness of a hydrogenation copolymer rises and flexibility is spoiled. the ratio of the block X occupied in a non-hydrogenation block copolymer when a non-hydrogenation block copolymer is a $n(A-B-X)$ type -- usually -- it is 30 or less % of the weight still more preferably 40 or less % of the weight preferably 50 or less % of the weight. Since the pliability of a hydrogenation block copolymer will fall if the block X exceeds 50 % of the weight, the flexibility of a solid electrolyte molding body falls. As for the ratio of the block A and the block B, it is desirable that it is within the limits of the above-mentioned in the portion except the block X. The hydrogenation rate of the block copolymer after hydrogenation needs to be not less than 90%. The melting point falls [a hydrogenation rate] at less than 90%, and heat resistance falls.

[0022]A hydrogenation block copolymer has the feature that the melting point which originates in the block A after hydrogenation at the elevated-temperature side, and the glass transition point which originates in the block B after hydrogenation at the low temperature side are shown. The melting point of a hydrogenation block copolymer is a factor which carries out a direct action to the heat resistance of the constituent of this invention, and is not less than 80 ** usually not less than 95 ** especially preferably not less than 85 ** preferably. In the melting point below 80 **, the heat resistance of a constituent is inferior and it becomes a problem practically. Although the maximum of the service temperature of an element is restricted by the boiling point of the

electrolyte used in the usual electrochemical element, in the case of the electrochemical element using the solid electrolyte as an electrolyte, the maximum of such service temperature will become higher. Since the activation energy of conduction of a solid electrolyte is generally high compared with the thing of a liquid electrolyte, at an elevated temperature, movement of the ion in an electrolyte will become quick and the electrochemical element using a solid electrolyte will show the characteristic which excelled what used the liquid electrolyte in the elevated temperature. Therefore, it is required for the heat resistance of the high molecular compound used to be high. In the case of the fuel cell using a proton conductivity solid electrolyte, etc., the temperature of an element may be about 100 °C by generation of heat under operation of an element. Therefore, as for the melting point of a hydrogenation block copolymer, it is more preferred that it is not less than 95 °C. moreover — the glass transition temperature by the side of the low temperature of a hydrogenation block copolymer is a factor which acts on the low-temperature characteristic of a constituent — usually -25 °C or less -30 °C or less is -35 °C or less especially preferably. When the glass transition temperature by the side of low temperature exceeds -25 °C, the kinetic property at the time of low temperature declines, and decline in the ionic conductivity by the side of the low temperature of a constituent also becomes large.

[0023]A hydrogenation block copolymer can be manufactured with a known technique. For example, it can manufacture by the method currently indicated by JP,4-342752,A. As a solid electrolyte in which the ion conductivity more than 10^{-4} S/cm is shown at a room temperature, the thing of copper-ion conductivity, silver ion conductivity, proton conductivity, and fluoride ion conductivity, etc. are found out until now. The lithium ion conductivity solid electrolyte attracts attention as an electrolyte for all the solid lithium cells especially. However, the lithium cell which generates high tension is equipped with the anode in which strong oxidizing power is shown, and the negative electrode in which strong reducing power is shown. Therefore, movement of ion is not barred, but even if the high molecular compound added by the electrolyte layer shows the characteristic which shows a high binding property, it may deteriorate by contact with these anodes or a negative electrode. The effect is the largest when the hydrogenation block copolymer by this invention constitutes a solid electrolyte molding body with a lithium ion conductivity solid electrolyte, since it is stable also to such an oxidation-reduction reaction.

[0024]When a lithium ion conductivity thing is taken for an example, a solid electrolyte The thing of crystalline substances, such as $\text{Li}_{1.3}\text{Sc}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ and $\text{Li}_{0.2}\text{La}_{0.6}\text{TiO}_3$. It is divided roughly into amorphous things, such as $\text{Li}_2\text{S}-\text{SiS}_2$. The thing of a crystalline substance has many which have anisotropy in the conductivity of ion, in order to realize high ion conductivity, it sinters a molding body, and the necessity of connecting an ion conduction course between solid electrolyte particles often produces it. To it, the ion conduction of a noncrystalline solid electrolyte is isotropic, and the ion conduction course between particles can be easily connected by the application-of-pressure molding method. Therefore, in the solid electrolyte molding body aiming at simplifying the composition process in constituting an electrochemical element, it is preferred to use an amorphous solid electrolyte. There are some which make a subject oxides, such as what makes sulfides, such as $\text{Li}_2\text{S}-\text{SiS}_2$, a subject, and $\text{Li}_2\text{O}-\text{SiO}_2$, in a lithium ion conductivity noncrystalline solid electrolyte. What makes a sulfide a subject has high reactivity, such as moisture, and also when mixing with a high molecular compound, there are the necessity of using the solvent of non-polarity etc. It is meltable to the solvent of non-polarity, and the hydrogenation block copolymer in this invention can be composite-ized, without spoiling the characteristic of the lithium-ion-conductivity noncrystalline solid electrolyte which made the sulfide the subject.

[0025]As a lithium-ion-conductivity inorganic solid electrolyte, high ion conductivity and the thing which has a large potential window are preferred, and especially the amorphous thing that made the sulfide the subject is preferred as what has these characteristics. As a lithium-ion-conductivity amorphous inorganic solid electrolyte which made the sulfide the subject, when a lithium sulfide and a silicon sulfide are made into the charge of a start material, it becomes what has the low steam pressure of the charge of a start material, and evapotranspiration of the charge of a start material at the time of solid electrolyte composition can be suppressed. Therefore, since the synthetic method of a solid electrolyte can be made simple, as a lithium-ion-conductivity amorphous inorganic compound, the thing containing silicon is used especially preferably. The mechanical strength of a lithium ion conductive solid electrolyte molded body can be further raised by adding the structure of electronic insulation. As an example of the structure of electronic insulation, textile fabrics, a nonwoven fabric, a porous film, etc. can be mentioned. As a method of manufacturing the solid electrolyte Plastic solid of this invention, the solution of a hydrogenation block copolymer is added to solid electrolyte powder, mixture dispersion is performed with a paint conditioner etc., and the slurry which solid electrolyte powder distributed in the solution of a hydrogenation block

copolymer is obtained. Subsequently, the method of carrying out coating of the slurry on a substrate with a mold-release characteristic, and acquiring the solid electrolyte Plastic solid of film state or the method of applying or impregnating electronic insulation structures, such as textile fabrics, with a slurry, and acquiring a sheet shaped solid electrolyte Plastic solid is mentioned.

[0026]Without barring movement of ion, when it composite-izes with other particles, the hydrogenation block copolymer by this invention can make the binding property between particles good, and can obtain a molding body with high processability. In the electrode used for an electrochemical element, an exchange of ion is performed between an electrode active material and an electrolyte. Since it is necessary to give high moldability to an electrode, without barring a motion of ion as stated previously, the electrode molding body which can be satisfied with using the hydrogenation block copolymer by this invention of these requests can be constituted. When a solid electrolyte is used as an electrolyte, in order to improve moldability, as it especially said previously that a binder is added, it has a problem to which an electrode reaction rate falls easily, and especially the effect using a hydrogenation block copolymer as a binder is large. The effect of using especially a hydrogenation block copolymer will become big from the anti-oxidation reduction nature of a binder becoming important as stated also in advance as an electrode active material in the case of the active material for lithium cells. In that case, an electrode molding body contains an electrode active material or an electrode active material, and a solid electrolyte, and the solid electrolyte used is a lithium ion conductivity thing. Since there is nothing amorphous in an ion conduction course as a lithium ion conductive solid electrolyte as for anisotropy, connection of the ion conduction course between an electrode active material and an electrolyte becomes easy. As an amorphous lithium ion conductive solid electrolyte, what made the sulfide the subject is especially used preferably from high ion conductivity and a large potential window being shown.

[0027]The mechanical strength of an electrode molding body can be further raised by adding a structure to an electrode molding body. Since electron conductivity inside an electrode can be made high especially as a structure, the structure which consists of a electron conductive substance is used especially preferably. Here, as an example of the structure which consists of a electron conductive substance which can be used, there are metallic meshes, such as stainless steel, titanium, copper, etc. The hydrogenation block copolymer used for this invention has the rubber-like block of an olefin skeleton with crystalline polyethylene similar structure blocks. Since the rubber-like block of an olefin skeleton has big free volume, it can absorb the volume change of the electrode active material under operation of an electrochemical element. Since crystalline polyethylene similar structure blocks give a binding property and flexibility strong between the constituent particles of an electrochemical element, the electrochemical element which solves the problem resulting from the fall of the junction nature between the particles by the volume change of an active material, and stabilizes and operates can be obtained.

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EXAMPLE

[Example]Hereafter, the example of this invention is described in detail. All of composition of the lithium-ion-conductivity inorganic solid electrolyte explained below and its ionic conductivity measurement were performed under dry argon atmosphere. First, the synthetic example of a hydrogenation block copolymer is explained. The structure and the characteristic of a hydrogenation block copolymer are shown in Table 1. A in the structural formula of an ingredient shows the block A among front, B shows the block B, and X shows a polystyrene block, respectively. A manufacturing method is shown below.[0029][Manufacture of a hydrogenation block copolymer (H-1)] 3.2 kg of cyclohexane and 1.2 kg of butadiene are taught to the autoclave of 20 l. of inner capacity, and 33 ml of 14-% of the weight tetrahydrofuran solutions of n-butyl lithium are added. Temperature up is carried out to about 70 **, 2.8 kg of butadiene and 108 ml of tetrahydrofurans are added further in the place where the appending rate became 100%, and a polymerization is continued at about 70 **. 26 ml adding and making the 20-% of the weight tetrahydrofuran solution of dichlorosilane react for about 20 minutes, when an appending rate will be 100% -- a jib -- coupling of the lock polymer was carried out and the triblock copolymer was obtained. After a polymerization is completed, reaction mixture shall be 70 ** and The n-butyl lithium 3g, 3 g of 2,6-di-t-butyl-p-cresol, 1g of bis(cyclopentadienyl)titanium dichloride, and 2 g of diethylaluminum chloride were added, and it was made to react by 10kg/cm of hydrogen pressure ² for 1 hour. This reaction mixture was dried with a roll after a steam strip, and the hydrogenation block copolymer (H-1) was obtained.

[A hydrogenation block copolymer (H-2) - (H-4) manufacture] So that it may become each hydrogenation block copolymer as shown in Table 1, Monomer species, a monomer amount, a catalyst amount, polymerization temperature, polymerization time, etc. were changed, and hydrogenation block copolymer (H-2) - (H-4) was obtained according to the hydrogenation block copolymer (H-1).

[0030]
[Table 1]

試料番号	H-1	H-2	H-3	H-4
成分の構造式	A-B-A	A-B-A	A-B-A	A-B-X
ブロック A の 1,2-ビニル結合含量(%)	12	13	12	13
ブロック A 量(重量%)	30 (15×2)	20 (10×2)	40 (20×2)	15
ブロック B の 1,2-ビニル結合含量(%)	42	41	65	42
ブロック B 量(重量%)	70	80	60	70
ブロック X 量(重量%)				15
特性				
水素添加率(%)	98	97	98.5	97.5
融点(高温側)	92	89	90	92
ガラス転移温度(低温側)	-52	-54	-55	-51
MFR (230℃×2.16kg)	10	5	8	0.5
分子量(×10 ⁴)	15	20	15	15

[0031]<<Example 1>> -- the sulfide glass of the lithium ion conductivity expressed with 0.6Li₂S-0.4SiS₂ as a solid electrolyte -- the lithium ion conductive solid electrolyte molded body was obtained, using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by 0.6Li₂S-0.4SiS₂ as a solid electrolyte was compounded. The silicon sulfide (SiS₂) was mixed with the lithium sulfide (Li₂S) at a rate of 0.6:0.4 by the mole ratio, and the mixture was put in the crucible of glassy carbon. The crucible was put in the vertical type furnace, it heated to 950 ** in the argon air current, and the mixture was made into the molten state. After 2-hour heating, crucible was dropped into liquid nitrogen, and was quenched, and the lithium-ion-conductivity noncrystalline solid electrolyte expressed with 0.6Li₂S-0.4SiS₂ was obtained. Thus, from the lithium-ion-conductivity noncrystalline solid electrolyte and hydrogenation block copolymer (H-1) which were obtained, the lithium ion conductive solid electrolyte molded body was obtained by the following method. First, the solid electrolyte obtained above was ground to 350 or less meshes. The toluene solution of (H-1) was added to this solid electrolyte powder, and it fully kneaded, and was considered as slurry form. It was made for the solid content of a hydrogenation block copolymer and the weight ratio of solid electrolyte powder to be set to 2:98 as for the mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the lithium ion conductive solid electrolyte molded body was obtained.

[0032]The ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the alternating-current-impedance method described below. First, the sheet of the lithium ion conductive solid electrolyte molded body obtained above was clipped to the discoid of 10 mmphi. The platinum board of 10 mmphi was welded by pressure to both sides of this disk, it was considered as the electrode for impedance measurement, and the ionic conductivity measuring cell was constituted. Alternating current impedance impressed and measured the volts alternating current of 10 mV with the vector impedance analyzer. As a result, the ionic conductivity of the obtained lithium ion conductive solid electrolyte molded body was 2.45x10⁻⁴S/cm.

When the hydrogenated block copolymer was not added as a comparative example, but pressing of the solid electrolyte powder was carried out and the ionic conductivity was measured similarly, it was $4.5 \times 10^{-4} \text{ S/cm}$. Next, the bending test was done in order to investigate that flexibility as evaluation of the processability of this lithium ion conductive solid electrolyte molded body. The bending test twisted this lithium ion conductive solid electrolyte molded body around the Indanthrene loess reinforcing bars of 50 mmphi, and viewed the state of the molding body. As a result, as for the lithium ion conductive solid electrolyte molded body in this example, it turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test. As mentioned above, it turned out that it has high lithium ion conductivity according to this invention, and the lithium ion conductive solid electrolyte molded body excellent in processability is obtained.

[0033]<<Example 2>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-2), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $2.8 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0034]<<Example 3>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-3), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $3.4 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0035]<<Example 4>> It replaced with having used in Example 1 as a hydrogenation block copolymer (H-1), and except having used (H-4), it is the same method as Example 1, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $2.5 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0036]<<Example 5>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-3) was used for Example 3 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte was compounded. First, the glass preform for compounding a noncrystalline solid electrolyte was compounded. The silicon sulfide (SiS_2) was mixed with the lithium sulfide (Li_2S) at a rate of 0.64:0.36 by the mole ratio, this mixture was put in glassy carbon crucible, and it fused at 950 ** among the horizontal type furnace. Then, the noncrystalline solid electrolyte which quenches melt with a congruence roller and is expressed with $0.64\text{Li}_2\text{S}-0.36\text{SiS}_2$ was obtained. This noncrystalline solid electrolyte was made into the glass preform, and lithium phosphate was mixed so that it might become the presentation of $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ after grinding. The lithium-ion-conductivity noncrystalline solid electrolyte which heats and quenches this mixture by the same method as the above, and is expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ was obtained.

[0037]0. replacing with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and using this solid electrolyte -- as a hydrogenation block copolymer -- Example 3 -- having used (H-3) -- the lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having used. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $5.3 \times 10^{-4} \text{ S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $7.8 \times 10^{-4} \text{ S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0038]<<Example 6>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.05\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-3) was used for Example 3 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. 0. The lithium-ion-conductivity noncrystalline solid

electrolyte expressed with $0.5\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ was compounded by the same method as Example 5 except having replaced with lithium phosphate and having used lithium oxide. using the obtained lithium ion conductive solid electrolyte -- as a hydrogenation block copolymer -- Example 3 -- having used (H-3) -- the lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having used. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $4.3 \times 10^{-4} \text{S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $6.6 \times 10^{-4} \text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0039]<<Example 7>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the lithium-ion-conductivity noncrystalline solid electrolyte expressed with the following methods by $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ as a lithium-ion-conductivity inorganic solid electrolyte was compounded. First, the noncrystalline solid electrolyte expressed with the same method as Example 1 by $0.5\text{Li}_2\text{S}-0.5\text{SiS}_2$ was obtained except having changed the mixture ratio of the starting material. This noncrystalline solid electrolyte was made into the glass preform, and after grinding, lithium iodide was mixed so that it might become the presentation of $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$. The lithium-ion-conductivity noncrystalline solid electrolyte which heats and quenches this mixture in a similar way again, and is expressed with $0.30\text{LiI}-0.35\text{Li}_2\text{S}-0.35\text{SiS}_2$ was obtained.

[0040]0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and having used this solid electrolyte. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured by the same method as Example 1, it was $3.5 \times 10^{-4} \text{S/cm}$. When solid electrolyte powder independent ionic conductivity was also measured by the same method as Example 1 as a comparative example, it was $7.2 \times 10^{-4} \text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also to the bending test done by the same method as Example 1.

[0041]<<Example 8>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, the phosphorus sulfide (P_2S_5) was mixed with the lithium sulfide (Li_2S) at a rate of 0.5:0.5 by the mole ratio as raw material of a solid electrolyte. This mixture was enclosed in the quartz tube, at 900 **, the quartz tube was dropped underwater, and was quenched after melting, and the noncrystalline solid electrolyte expressed with $0.5\text{Li}_2\text{S}-0.5\text{P}_2\text{S}_5$ was obtained. 0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6\text{Li}_2\text{S}-0.4\text{SiS}_2$, and having used this solid electrolyte. The place which measured the ionic conductivity of the solid electrolyte powder which is this lithium ion conductive solid electrolyte molded body and a comparative example by the same method as Example 1, The ionic conductivity of the solid electrolyte molding body which added the hydrogenation block copolymer is $1.0 \times 10^{-4} \text{S/cm}$, and the fall rate had fitted in less than 1/2 as compared with solid electrolyte independent $1.6 \times 10^{-4} \text{S/cm}$. It turned out that abnormalities are not seen but the exterior has high flexibility also to the bending test done by the same method as Example 1.

[0042]<<Example 9>> the lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{B}_2\text{S}_3$ as a lithium-ion-conductivity inorganic solid electrolyte, (H-1) was used for Example 1 and the appearance as a hydrogenation block copolymer, respectively, and the lithium ion conductive solid electrolyte molded body was constituted. The details are shown below. First, as raw material of a solid electrolyte, The noncrystalline solid electrolyte expressed with the same method as Example 8 by $0.6\text{Li}_2\text{S}-0.4\text{B}_2\text{S}_3$ was obtained except having used

what mixed boron sulfide (B_2S_3) with the lithium sulfide (Li_2S) at a rate of 0.6:0.4 by the mole ratio. 0. The lithium ion conductive solid electrolyte molded body was obtained by the same method as Example 1 except having replaced with the solid electrolyte expressed with $6Li_2S-0.4SiSB_2$, and having used this solid electrolyte. The place which measured the ionic conductivity of the solid electrolyte powder which is this lithium ion conductive solid electrolyte molded body and a comparative example by the same method as Example 1, The ionic conductivity of the solid electrolyte molding body which added the hydrogenation block copolymer is $1.2 \times 10^{-4} S/cm$, and the fall rate had fitted in less than 1/2 as compared with solid electrolyte independent $1.9 \times 10^{-4} S/cm$. It turned out that abnormalities are not seen but the exterior has high flexibility also by the bending test done by the same method as Example 1.

[0043]<<Example 10>> the noncrystalline solid electrolyte expressed with $0.6Li_2S-0.4SiS_2$ like Example 1 as a lithium ion inorganic solid electrolyte, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium-ion-conductivity inorganic solid electrolyte and a hydrogenation block copolymer were obtained using (H-3) as a hydrogenation block copolymer. The details are shown below. From the lithium-ion-conductivity inorganic solid electrolyte obtained in Example 1, and (H-3), the lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained. the composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are boiled and shown in Table 2. The result of a bending test is also shown in Table 2.

[0044]
[Table 2]

共重合体比率 (wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4} S/cm$)	4.1	3.8	3.4	2.8	2.0
折り曲げ試験	良好	良好	良好	良好	良好
注			実施例 3		

[0045]It turns out that it excels in flexibility and the lithium ion conductive solid electrolyte molded body whose ionic conductivity is also very high is simultaneously obtained also with a little additions by using a hydrogenation block copolymer from this result. Even if it adds a hydrogenation block copolymer comparatively so much, the fall of ionic conductivity also has the small feature.

[0046]<<Example 11>> the noncrystalline solid electrolyte expressed with $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$ obtained in Example 5 as a lithium-ion-conductivity inorganic solid electrolyte, The lithium ion conductive solid electrolyte molded body was obtained using a polyethylene mesh as a structure of further electronic insulation using (H-3) respectively as a hydrogenation block copolymer. The details are shown below. The slurry containing a solid electrolyte and a specific polymer was obtained by the same method as Example 1. Then, with the doctor blade method, the opening of the polyethylene mesh of 70% of a numerical aperture was filled up with this slurry. Then, it dried under decompression of 40 **, toluene was evaporated, and the lithium ion conductive solid electrolyte molded body was obtained. When the ionic conductivity of this lithium ion conductive solid electrolyte molded body was measured like Example 1, it was $3.0 \times 10^{-4} S/cm$. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen as for an exterior, and abnormalities are not seen by the bending test using the stainless steel stick of 5 more mmphi, either, but the lithium ion conductor by this example has higher flexibility. As mentioned above, according to this invention using a lithium-ion-conductivity inorganic

solid electrolyte, a hydrogenation block copolymer, and the structure of further electronic insulation, it turned out that it has high processability and a lithium ion conductive solid electrolyte molded body with high lithium ion conductivity is obtained especially.

[0047]<<Example 12>> as a lithium-ion-conductivity inorganic solid electrolyte. The lithium-ion-conductivity noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ which was replaced with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ used in Example 11, and was obtained in Example 1, moreover -- as a hydrogenation block copolymer -- Example 11 -- having used (H-3) -- replacing with (H-1) -- it using, respectively and, The lithium ion conductive solid electrolyte molded body consisted of the same methods as Example 11 except having replaced with the polyethylene mesh used in Example 11, and having used the mesh of glass fiber as an electronic insulation structure. When the ionic conductivity of the lithium ion conductive solid electrolyte molded body obtained as a result was measured like Example 1, it was $3.3\times 10^{-4}\text{S/cm}$. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen as for an exterior, and abnormalities are not seen by the bending test using the stainless steel stick of 5 more mmphi, either, but it has flexibility with a higher lithium ion conductive solid electrolyte molded body by this example.

[0048]<<the comparative example 1>> -- the styrene ethylene butylene styrene block copolymer (the product made from SHELL.) which does not have a crystalline block structure It expresses with trade name KRATON G1652 and the following SEBS. It uses, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium ion electrical transmission nature inorganic solid electrolyte and SEBS were obtained using the noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ like Example 1 as a lithium-ion-conductivity inorganic solid electrolyte. The details are shown below. The lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained from the lithium-ion-conductivity inorganic solid electrolyte obtained in SEBS and Example 1. The composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are shown in Table 3. The result of a bending test is also shown in Table 3.

[0049]
[Table 3]

S E B S 共重合体比率 (wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4}\text{S/cm}$)	—	—	—	0.9	0.5
折り曲げ試験	成型体として回収不可	成型体として回収不可	成型体として回収不可	ひび割れ発生	良好
注	成型体として回収不可のため伝導度測定不可				

[0050]<<Comparative example 2>> 5 % of the weight of styrene and 95 % of the weight of butadiene are polymerized, The copolymer (it expresses with H-SBR below.) produced by the 1,2-vinyl bond content of butadiene hydrogenating the styrene butadiene random copolymer which is 80% is used, Various lithium ion conductive solid electrolyte molded bodies which changed the composition ratio of a lithium-ion-conductivity inorganic solid electrolyte and H-SBR were obtained using the noncrystalline solid electrolyte expressed with $0.6\text{Li}_2\text{S}-0.4\text{SiS}_2$ like Example 1 as a lithium ion inorganic solid electrolyte. The details are shown below. The lithium ion conductive solid electrolyte molded body which changed composition ratio by the same method as Example 1 was obtained from the lithium-ion-conductivity inorganic solid electrolyte obtained in H-SBR and Example 1. The composition ratio of a lithium ion conductive solid electrolyte molded body and the relation of ionic conductivity are shown in Table 4. The result of a bending test is also shown in Table 4.

[0051]
[Table 4]

H-SBR 比率(wt%)	0.4	1.0	2.0	3.5	5.0
固体電解質比率 (wt%)	99.6	99.0	98.0	96.5	95.0
イオン伝導度 ($\times 10^{-4}$ S/cm)	—	—	—	—	0.4
折り曲げ試験	成型体として回収不可	成型体として回収不可	成型体として回収不可	成型体として回収不可	良好
注	成型体として回収不可のため伝導度測定不可				

[0052]When processability is good, and is rich in flexibility and the hydrogenation block copolymer of this invention which has a crystalline block obtains the lithium ion conductive solid electrolyte molded body of high ion conductivity by comparison with the above example and a comparative example, it turns out that it is a suitable material.

[0053]<<Example 13>> In this example, the proton conductivity solid electrolyte molding body was produced, using (H-1) respectively as the silica gel which doped phosphoric acid as a solid electrolyte of proton conductivity, and a hydrogenation block copolymer. First, the silica gel which doped phosphoric acid was compounded by the following methods. It diluted with ethanol, using a tetraethoxysilane (it expresses with the following TEOS.) as a starting material for compounding silica gel. It was made for the mixture ratio of TEOS and ethanol to be set to 1:4 by a mole ratio at this time. In this solution, it is a rate of 8 and 0.01 in the mole ratio to TEOS, respectively, and in addition, pure water and tetraethylammonium tetrafluoroborate were stirred for 5 minutes so that a 3.6wt% hydrochloric acid aqueous solution might be set to 0.01 by the mole ratio of HCl to TEOS. Then, the 85wt% phosphoric acid aqueous solution was added so that it might be set to TEOS:H₃PO₄=1:0.5, and it stirred in the well-closed container for 3 hours. Subsequently, it was neglected for 5 hours, gelled, it heated at 150 ** for 2 hours, and the silica gel which doped phosphoric acid was obtained.

[0054]The silica gel which doped the phosphoric acid obtained as mentioned above was ground, and it stirred in the toluene solution of (H-1). However, it was made for the ratio of the solid electrolyte of proton conductivity to the solid content of a copolymer (H-1) to be set to 19:1 by a weight ratio. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, it dried under decompression of 100 **, and toluene was evaporated. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the proton conductivity solid electrolyte molding body was obtained. Thus, when the ionic conductivity of the obtained proton conductivity solid electrolyte molding body was measured by the same alternating-current-impedance method as Example 1, the value of 3.2×10^{-3} S/cm was shown. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen but the exterior has flexibility with a higher proton conductivity solid electrolyte molding body by this example. As mentioned above, according to this invention using a proton conductivity inorganic solid electrolyte and a hydrogenation block copolymer, it turned out that it has high processability and a proton conductivity solid electrolyte molding body with high proton conductivity is obtained.

[0055]<<Example 14>> In this example, the silver ion conductivity solid electrolyte molding body was produced using the solid electrolyte expressed with Ag₆I₄WO₄ as a silver ion conductivity solid electrolyte, using (H-1) as a hydrogenation block copolymer. First, Ag₆I₄WO₄ was compounded by the following methods. As a starting material, silver iodide (AgI), silver oxide (Ag₂O), and tungstic oxide (WO₃) were used. These starting materials were mixed, and melting was heated and carried out at 400 ** in the quartz crucible. The silver ion conductivity solid electrolyte which cools radiationally in a furnace after that and is expressed with Ag₆I₄WO₄ was obtained.

[0056]Thus, the obtained silver ion conductivity solid electrolyte was ground, and it stirred in the toluene solution of (H-1). However, it was made for the ratio of the solid electrolyte of silver ion conductivity to the solid content

of a copolymer (H-1) to be set to 97:3 by a weight ratio. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, it dried under decompression of 100 **, and toluene was evaporated. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and the silver ion conductivity solid electrolyte molding body was obtained. Thus, the ionic conductivity of the silver ion conductivity solid electrolyte in the obtained silver ion conductivity solid electrolyte molding body and the state where a hydrogenation block copolymer is not added for comparison was measured by the same alternating-current-impedance method as Example 1. As a result, silver ion conductivity solid electrolyte independent ionic conductivity was $4.0 \times 10^{-2} \text{ S/cm}$. On the other hand, in what added the hydrogenation block copolymer, it is $2.3 \times 10^{-2} \text{ S/cm}$ and 1/less than 2 had been the ion-conductive fall rate as compared with the former. In the bending test done by the same method as Example 1, it turned out that abnormalities are not seen but the exterior has flexibility with a higher silver ion conductivity solid electrolyte molding body by this example.

[0057]<<Example 15>> The electrode molding body was obtained for the lithium cobalt oxide expressed with LiCoO_2 which is an electronic-lithium ion mixed conductor as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte, using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. First, LiCoO_2 was compounded weighing and by mixing and calcinating at 900 ** among the atmosphere so that it might become a ratio of $\text{Co/Li}=1$ about cobalt oxide (Co_3O_4) and lithium carbonate (Li_2CO_3). Thus, the electrode molding body was obtained by the following method from obtained LiCoO_2 and (H-1). First, LiCoO_2 obtained above was ground to 350 or less meshes. The toluene solution of (H-1) was added to this LiCoO_2 powder, and it fully kneaded, and was considered as slurry form. It was made for the solid content of a hydrogenation block copolymer and the weight ratio of LiCoO_2 powder to be set to 5:95 as for the mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and diameter 10mmphi and a 0.2-mm-thick electrode molding body were obtained by clipping after that. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the water dispersion of poly ethylene tetrafluoride (it expresses with PTFE below.). Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the LiCoO_2 was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0058]Thus, the following alternating-current-impedance method estimated the electrochemical characteristic of the obtained electrode molding body. The outline composition of a measuring device is shown in drawing 1. One expresses a sample electrode holder among a figure. This electrode holder was made to weld the electrode molding body 2 by pressure to the lead terminal 3, and it set to it, and was made it with the examination pole. This examination pole was immersed into the electrolysis solution 4 in the container 7. An electrolysis solution dissolves 6 lithium-fluoride phosphorus (LiPF_6) in the mixed solvent which mixed propylene carbonate and dimethoxyethane at a rate of the volume ratio 1:1 so that it may become the concentration of 1.0M. It was immersed into the electrolysis solution at the reference pole 5 and the counter electrode 6 using the foil of metal lithium, respectively. In this way, it was considered as the measuring cell. With the impedance analyzer, the volts alternating current of 10 mV was impressed to such a measuring cell, and alternating-current-impedance measurement was performed to it in the frequency range (100 kHz - 1 mHz).

[0059]As a result, when the electrode molding body obtained without adding a binder was used, the moldability of the electrode was bad, during measurement, LiCoO_2 which is an electrode active material dropped out in the electrolysis solution, and impedance was not able to be measured. The impedance spectrum acquired about the thing using PTFE which is a hydrogenation block copolymer by this invention and a comparative example as a binder was shown in drawing 2. When the specific polymer by this invention was used as a binder so that more clearly than this figure, it turned out that the electrode molding body which impedance shows a low value and shows the high electrode reaction characteristic is obtained. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0060]<<Example 16>> It replaced with having used in Example 15 as a hydrogenation block copolymer polymer (H-1), and except having used (H-2), it is the same method as Example 15, and the electrode molding body was

obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 310ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0061]<<Example 17>> It replaced with having used in Example 15 as a hydrogenation block copolymer (H-1), and except having used (H-3), it is the same method as Example 15, and the electrode molding body was obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 270ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0062]<<Example 18>> It replaced with having used in Example 15 as a hydrogenation block copolymer (H-1), and except having used (H-4), it is the same method as Example 15, and the electrode molding body was obtained. The result of having performed alternating-current-impedance measurement by the method same as an electrode characteristic of this electrode molding body as Example 15, The value of the impedance in 10 mHz is 420ohms, and it turned out that impedance lower than the electrode molding body using PTFE as a binder of the comparative example in Example 15 is shown.

[0063]<<Example 19>> Replace with the lithium cobalt oxide expressed with LiCoO_2 used in Example 15 as an electronic-lithium ion mixed conductor, and LiNiO_2 (H-2) was used for Example 16 and the appearance as a hydrogenation block copolymer, respectively, and the electrode molding body was constituted. The details are shown below. First, lithium hydroxide was mixed with nickel oxide (NiO), and LiNiO_2 was compounded by heating at 800 ** among the atmosphere. Next, LiNiO_2 obtained above was ground to 350 or less meshes. The electrode molding body was obtained by the same method as Example 15 using this LiNiO_2 powder and the toluene solution of (H-2). For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the toluene solution of block copolymer SEBS used by the comparative example 1. Binders, such as a specific polymer, were not added for comparison, but pressing of the LiNiO_2 was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained. Thus, the same alternating-current-impedance method as Example 15 estimated the electrochemical characteristic of the obtained electrode molding body.

[0064]As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, LiNiO_2 which is an electrode active material dropped out in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed the thing using SEBS which are a hydrogenation block copolymer by this invention, and a comparative example as a binder, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 450ohms in 10 mHz, In the electrode molding body using SEBS in a comparative example, it is 740ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0065]<<Example 20>> as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, the lithium manganic acid ghost expressed with LiMn_2O_4 -- as a hydrogenation block copolymer -- Example 16 -- being the same (H-2) -- it used, respectively and the electrode molding body was constituted. The details are shown below. LiMn_2O_4 mixed manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2$) with lithium carbonate (Li_2CO_3), and compounded it by heating at 750 ** among the atmosphere. Next, LiMn_2O_4 obtained above was ground to 350 or less meshes. Graphite powder was mixed with this LiMn_2O_4 powder at a rate of 9:1 by the weight ratio as a electron conductive substance. The electrode molding body was obtained by the same method as Example 15 using the toluene solution [further / (H-2)]. However, it was made for the solid content of a hydrogenation block copolymer and the weight ratio of LiMn_2O_4 powder to be set to 5:95 as for the mixture ratio at the time of kneading. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the water dispersion of PTFE. Binders,

such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiMn_2O_4 powder and black lead was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0066] Thus, the same alternating-current-impedance method as Example 15 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, LiMn_2O_4 which is an electrode active material dropped out in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed the thing using PTFE which is a hydrogenation block copolymer by this invention, and a comparative example as a binder, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 570ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 810ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0067] <<Example 21>> Graphite fluoride was used as a substance in which an electrochemical reduction reaction is shown in the electrolyte which has lithium ion conductivity, (H-2) was used for Example 16 and the appearance as a hydrogenation block copolymer, respectively, and the electrode molding body was constituted. The details are shown below. Graphite fluoride was compounded by heating graphite powder at 600 ** among fluorine gas. Thus, except having replaced the obtained graphite fluoride with LiMn_2O_4 and having used it, the electrode molding body for the electrode molding body by this invention and comparison was formed like Example 20, and the electrochemical characteristics were investigated. As a result, when the electrode obtained without adding a binder was molded, the moldability of the electrode was bad, during measurement, the graphite fluoride which is an electrode active material was omitted in the electrolysis solution, and impedance was not able to be measured. The result of the alternating-current-impedance measurement which followed as a binder the hydrogenation block copolymer by this invention, and the electrode molding body using PTFE which is a comparative example, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 770ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 890ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0068] <<Example 22>> It replaced with LiCoO_2 , and as a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, except having used natural graphite, the electrode molding body was constituted like Example 16, and the electrode characteristic was investigated. As a result, the electrode molding body obtained without adding a binder had the bad moldability of the electrode, and during measurement, natural graphite which is an electrode active material was omitted in the electrolysis solution, and it was not able to measure impedance. The result of the alternating-current-impedance measurement which followed as a binder the hydrogenation block copolymer by this invention, and the electrode molding body using PTFE which is a comparative example, As opposed to the impedance of the electrode molding body using the hydrogenation block copolymer by this invention as a binder having been 370ohms in 10 mHz, In the electrode molding body using PTFE in a comparative example, it is 520ohms and it turned out that the electrode molding body the direction of the electrode molding body by this invention indicates low impedance to be, and indicates the high electrode reaction characteristic to be is obtained.

[0069] <<Example 23>> LiCoO_2 obtained in Example 15 as an electronic-lithium ion mixed conductor, The electrode molding body was obtained for the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ obtained in Example 5 as a lithium-ion-conductivity inorganic solid electrolyte, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. The electrode molding body was obtained by the following method from the solid electrolyte obtained in Example 5, and LiCoO_2 and the hydrogenation block copolymer (H-2) which were obtained in Example 15. First, the solid electrolyte obtained above was ground to 350 or less meshes. This solid electrolyte powder, LiCoO_2 powder, and the toluene solution of (H-2) were fully kneaded, and it was considered as slurry form. It was made for the weight ratio of the solid content of a hydrogenation block copolymer, solid electrolyte powder, and LiCoO_2 powder to be set to 1:32:67 as for the

mixture ratio at the time of kneading. Thus, the obtained slurry was applied on the fluoro-resin board with the doctor blade method, and under decompression of 100 **, toluene was evaporated and it dried. It exfoliated from the fluoro-resin board after desiccation of 3 hours, and diameter 10mmphi and a 0.2-mm-thick electrode molding body were obtained by clipping after that. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was similarly obtained using the toluene solution of SEBS used by the comparative example 1. Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiCoO_2 and a solid electrolyte was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0070] Thus, the following alternating-current-impedance method estimated the electrochemical characteristic of the obtained electrode molding body. The outline composition of a measuring device is shown in drawing 3. 11 express the hollow sample electrode holder made from polyethylene terephthalate among a figure. The lead terminal 13 was made to weld the electrode molding body 12 by pressure to this electrode holder, and it was considered as the examination pole. This examination pole and the counter electrode 15 which welds metal lithium foil by pressure to the lead terminal 14 were molded into one via the above-mentioned lithium ion conductive solid electrolyte 16, and was used as the measuring cell. With the impedance analyzer, the volts alternating current of 10 mV was impressed to such a measuring cell, and alternating-current-impedance measurement was performed to it in the frequency range (100 kHz - 1 mHz).

[0071] The impedance spectrum acquired as a result was shown in drawing 4. When the hydrogenation block copolymer by this invention is used as a binder so that more clearly than this figure, Although it was high when compared with what did not use a binder, it turned out that the electrode molding body which shows impedance lower than the case where SEBS is used as a binder, and shows the high electrode reaction characteristic is obtained. Next, the drop test estimated the moldability of these electrode molding bodies. From 50 cm in height, the drop test dropped the electrode molding body on the board of marble, and observed the situation of the electrode molding body after fall. As a result, although abnormalities were not looked at by the molding body about the thing using the hydrogenation block copolymer by this invention as a binder, and the thing using SEBS as a binder, the molding body was cracked about what did not use a binder. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0072] <<Example 24>> LiNiO_2 obtained in Example 19 as an electronic-lithium ion mixed conductor, As a lithium-ion-conductivity inorganic solid electrolyte. The noncrystalline solid electrolyte expressed with $0.05\text{Li}_2\text{O}-0.60\text{Li}_2\text{S}-0.35\text{SiS}_2$ which was replaced with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ obtained in Example 5, and was obtained in Example 6, The electrode molding body was obtained using (H-1) respectively as a hydrogenation block copolymer. The details are shown below. The electrode molding body was obtained by the solid electrolyte obtained in Example 6, LiNiO_2 obtained in Example 19, and the method more nearly same than a hydrogenation block copolymer (H-1) as Example 23. Furthermore, for comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was obtained in a similar manner using the toluene solution of SEBS. Binders, such as a hydrogenation block copolymer, were not added for comparison, but pressing of the mixture of LiNiO_2 and a solid electrolyte was carried out to diameter 10mmphi and 0.2-mm-thick discoid, and the electrode molding body was obtained.

[0073] Thus, the same alternating-current-impedance method as Example 23 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the impedance at 10 mHz at the time of using the hydrogenation block copolymer by this invention as a binder was $3.3 \times 10^3 \Omega$. When a binder was not used and SEBS was used as $1.7 \times 10^3 \Omega$ and a binder to it, it was $5.4 \times 10^3 \Omega$. Although the electrode molding body by this example was high when it was compared with what did not use a binder, it turned out that the electrode molding body which shows a value lower than the case where SEBS is used as a binder, and shows the high electrode reaction characteristic is obtained. Next, when the same method as Example 23 estimated the moldability of these electrode molding bodies, abnormalities were not looked at by the molding body about the thing using the hydrogenation block copolymer by this invention as a binder, and the thing using SEBS as a binder, but. The molding body was cracked about what did not use a binder.

[0074] <<Example 25>> It replaces with the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ used in Example 23 as a lithium-ion-conductivity inorganic solid electrolyte, The electrode molding body

was constituted like Example 23 except having used the lithium ion conductive solid electrolyte of the crystalline substance expressed with $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$. The details are shown below. As raw material of a solid electrolyte, lithium carbonate, an aluminum oxide, titanium oxide, and orthophosphoric acid were used. After mixing these starting materials, the lithium-ion-conductivity inorganic solid electrolyte of the crystalline substance which carries out application-of-pressure molding at a pellet type, calcinates at 1300 ** for 24 hours, and is expressed with $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ was obtained. 0. The electrode molding body was obtained by the same method as Example 23 except having replaced with the noncrystalline solid electrolyte expressed with $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, and having used this solid electrolyte. Furthermore, for comparison, it replaced with the hydrogenation block copolymer used by this example, and the electrode molding body was obtained in a similar manner using the water dispersion of PTFE.

[0075] Thus, the same alternating-current-impedance method as Example 23 estimated the electrochemical characteristic of the obtained electrode molding body. As a result, the impedance of the electrode molding body using a hydrogenation block copolymer is $2.8 \times 10^3 \Omega$ in 10 mHz.

The impedance of the electrode molding body using PTFE was $4.8 \times 10^3 \Omega$.

It turned out that the electrode molding body using the hydrogenation block copolymer by this invention as a binder shows lower impedance from the above result. Next, as for no electrode molding bodies using the thing using the hydrogenation block copolymer by this invention as a binder, and PTFE as a binder, the molding body was destroyed when the same method as Example 23 estimated the moldability of these electrode molding bodies. As mentioned above, it turned out that it has the high electrode reaction characteristic according to this invention, and the electrode molding body excellent in moldability is obtained.

[0076] <<Example 26>> The electrode molding body was further obtained for the lithium cobalt oxide expressed with LiCoO_2 used in Example 15 as an electronic-lithium ion mixed conductor, using a polyethylene mesh as a structure, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. The slurry containing LiCoO_2 and a hydrogenation block copolymer was obtained by the same method as Example 15. Then, the opening of the polyethylene mesh of 70% of a numerical aperture was filled up with this slurry with the doctor blade method. Then, toluene was evaporated under decompression of 120 **, it dried, and the electrode molding body was obtained. When the alternating current impedance of this electrode molding body was measured like Example 15, the almost same impedance as the electrode molding body obtained in Example 15 was shown.

[0077] Next, the bending test was done in order to investigate that flexibility as evaluation of the moldability of this electrode molding body. The bending test twisted this electrode molding body around the stainless steel stick with a diameter [ϕ] of 40 mm, and viewed the state of the molding body. As a result, as for it, the electrode molding body in this example turned out that abnormalities are not seen but the exterior has high flexibility also by this bending test. The molding body was cracked when the same bending test was done to the electrode molding body obtained in Example 15 to it. As mentioned above, according to the substance and this invention using a structure further which show an electrochemical oxidation-reduction reaction in a hydrogenation block copolymer and the electrolyte which has lithium ion conductivity, it turned out that an electrode molding body with high moldability and the high electrochemical reaction characteristic is obtained especially.

[0078] <<Example 27>> LiNiO_2 which was replaced with LiCoO_2 used in Example 26 as an electronic-lithium ion mixed conductor, and was obtained in Example 19, The electrode molding body consisted of the same methods as Example 26 except having replaced with the polyethylene mesh used in Example 26, and having used the mesh made from stainless steel as a structure of electron conductivity as a structure like Example 26, as a hydrogenation block copolymer, using H-2 respectively. When the alternating current impedance of this electrode molding body is measured like Example 15, it is 390 ohms in value, and impedance lower than the electrode molding body obtained in Example 19 was shown. Next, the bending test was done in order to investigate that flexibility as evaluation of the moldability of this electrode molding body. The bending test twisted this electrode molding body around the Indanthrene loess reinforcing bars of 40 mmphi, and viewed the state of the molding body. As a result, as for it, the electrode molding body in this example turned out that abnormalities are not seen but the exterior has high flexibility also by this bending test.

[0079] <<Example 28>> The electrode molding body obtained in Example 15 as an anode, the electrode molding body obtained in Example 22 as a negative electrode, The lithium cell was obtained using respectively the lithium-ion-conductivity electrolyte which dissolved 6 lithium-fluoride phosphorus (LiPF_6) in the mixed solvent of

propylene carbonate and dimethoxyethane as a lithium ion conductivity electrolyte. The details are shown below. First, the anode molding body and the negative-electrode molding body were obtained by clipping the electrode molding body obtained in the electrode molding body and Example 22 which were acquired in Example 15. The lithium ion conductivity liquid electrolyte dissolved 6 lithium-fluoride phosphorus in the mixed solvent which mixed propylene carbonate and dimethoxyethane at a rate of the volume ratio 1:1 so that it might become the concentration of 1.0M, and it prepared it. The lithium cell with SEBARETA made from porous polyethylene made to intervene between the above-mentioned anode molding body, a negative-electrode molding body, and both and the section shown in drawing 5 using the lithium-ion-conductivity electrolyte was constituted. In drawing 5, 21 expresses the anode molding body arranged in the center of the cell case 24. After allotting the separator 23 and the negative-electrode molding body 22 and dropping the lithium-ion-conductivity electrolyte on this anode molding body 21, the whole was closed with the battery lid 26 via the gasket 25.

[0080]For comparison, it replaced with the anode molding body and negative-electrode molding body which were used by this example, and the lithium cell consisted of Example 15 and Example 22 using an anode molding body and a negative-electrode molding body using PTFE obtained for comparison as a binder. For comparison, it replaced with the hydrogenation block copolymer used by this example, and the lithium cell consisted of following methods, using a solid polymer electrolyte as a binder. As a solid polymer electrolyte, lithium perchlorate (LiClO₄) / polyethylene oxide (PEO) system was used. First, polyethylene oxide (it expresses with the following PEO.) was dissolved in acetonitrile, and LiClO₄ was dissolved further. However, it was made, as for the mixture ratio of PEO and LiClO₄, for lithium in LiClO₄ to serve as 1/50 of ratios to oxygen in PEO. Thus, the lithium cell consisted of the same methods as the above except having used the obtained solution.

[0081]Thus, the constituted lithium cell was charged to 4.2V with the current value of 1 mA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 1 mA in the voltage range of 3.0V-4.2V. As a result, in the lithium cell using a solid polymer electrolyte, abnormalities were observed in the charging curve during charge of a cell. In order to explore the cause, when the cell was disassembled, no positive and negative poles stopped the shape at the time of battery construction, but the electrode was swelling remarkably, and the current collection nature of the active material was lost. This is considered that the moldability of the electrode was lost when the solid polymer electrolyte dissolved into the electrolyte. Below, service capacity [in / for the internal impedance of the cell obtained by the above-mentioned examination as a binder about the lithium cell using the hydrogenation block copolymer by this invention and the lithium cell using PTFE as a binder / to Table 5 / each charging and discharging cycle] is shown in drawing 6, respectively. Although the fall of the service capacity accompanying a charging and discharging cycle was not observed about which lithium cell, either, it turns out that the direction of the lithium cell using the hydrogenation block copolymer by this invention shows low internal impedance, and serves as a cell also with big service capacity. According to this invention, it turned out that the moldability of an electrode can be improved and the lithium cell in which the outstanding battery characteristic is shown is obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0082]
[Table 5]

電池	内部インピーダンス (Ω)
水素添加ブロック共重合体使用	62
P T F E 使用	102

[0083]<<Example 29>> Except having used the electrode molding body obtained in Example 16 as an electrode molding body used for an anode, it was the same method as Example 28, and the lithium cell by this invention was constituted and the characteristic was evaluated. As a result, the lithium cell which added the hydrogenation block copolymer by this invention, 64-ohm internal impedance was indicated to be the service capacity of 14 or more mAh, and high service capacity and low internal impedance were shown compared with the lithium cell which

used PTFE as a binder and constituted it from Example 28 for comparison.

[0084]<<Example 30>> Except having used the electrode molding body obtained in Example 19 as an electrode molding body used for an anode, it was the same method as Example 28, and the lithium cell by this invention was constituted and the characteristic was evaluated. For comparison, the lithium cell was constituted using the electrode molding body which used SEBS for the binder of the comparative example in Example 19 as an anode, and the characteristic was evaluated. As a result, the service capacity of the lithium cell which added the hydrogenation block copolymer according to this invention is 18mAh.

Internal impedance was 87ohms.

To it, with the lithium cell constituted using SEBS of a comparative example as a binder, service capacity is 16mAh, internal impedance is 98ohms, and the direction of the lithium cell by this invention showed high service capacity and low internal impedance.

[0085]<<Example 31>> The electrode molding body constituted from the same method as Example 15 except having used the titanium disulfide which replaces with the lithium cobalt oxide expressed with LiCoO_2 , and is expressed with TiS_2 as positive active material Anode, It replaced with the natural graphite used in Example 29 as negative electrode active material, and the lithium cell was constituted, using metal lithium respectively. The details are shown below. First, TiS_2 was compounded with the CVD method from titanium metal and sulfur. Next, TiS_2 obtained above was ground to 350 or less meshes. This TiS_2 powder was replaced with LiCoO_2 powder, and was used, and the electrode molding body was obtained by the same method as Example 15. The lithium cell by this invention consisted of the same methods as Example 29 except having used this electrode molding body for the anode, and having used metal lithium foil for the negative electrode, respectively. It replaced with the hydrogenation block copolymer (H-1) for comparison, and the lithium cell using PTFE was also constituted.

[0086]Thus, the constituted lithium cell was discharged to 1.8V with the current value of 500microA. After discharge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 500microA in the voltage range of 1.8V-2.8V. As a result, the lithium cell using the hydrogenation block copolymer by this invention was [28mAh and internal impedance] 74ohms in discharge quantity of electricity. In the thing using PTFE to it, discharge quantity of electricity was 23mAh, and internal impedance was 86ohms. It turned out that the direction of the cell by this invention shows low internal impedance, and serves as a cell also with big service capacity from the above result.

[0087]<<Example 32>> Except having used as an anode the electrode molding body obtained in Example 20, it is the same method as Example 29, and the lithium cell was constituted. For comparison, except having used the electrode molding body using PTFE of the comparative example in Example 16 as a binder as an anode, it was the same method as the above, and the lithium cell was constituted and the characteristic was evaluated. As a result, the lithium cell using the hydrogenation block copolymer by this invention was [11mAh and internal impedance] 230ohms in service capacity. On the other hand, in the thing using PTFE, service capacity was 8.5mAh and internal impedance was 340ohms. It turned out that the direction of the cell by this invention shows low internal impedance, and serves as a cell also with big service capacity from this result.

[0088]<<Example 33>> Except having used the electrolyte which dissolved LiClO_4 in the mixed solvent of propylene carbonate and dimethoxyethane as a lithium ion conductivity electrolyte, it is the same method as Example 29, and the lithium cell by this invention and the lithium cell for comparison were constituted. As a result, the service capacity and internal impedance of the lithium cell using the hydrogenation block copolymer by this invention are 13mAh and 67ohms, respectively.

In the cell using PTFE to it, they were 11mAh and 71ohms, respectively.

[0089]<<Example 34>> The electrode molding body using the mesh made from stainless steel obtained in Example 27 in order to improve the moldability of an electrode further as an anode is used, Except having used the negative-electrode molding body using the mesh made from stainless steel furthermore indicated below, it is the same method as Example 28, and the lithium cell was constituted. The negative-electrode molding body was obtained by filling up the mesh made from stainless steel with the natural graphite obtained in Example 22, and the slurry containing (H-2), evaporating toluene under decompression of 100 **, and drying. Thus, the lithium cell consisted of the same methods as Example 28, using the obtained negative-electrode molding body and the electrode molding body obtained in Example 27 as an anode. Thus, the place which estimated the characteristic of

the constituted lithium cell as Example 28 similarly, The service capacity of the lithium cell using the structure which the fall of the service capacity accompanying a charging and discharging cycle was not observed, but was further obtained by this example 17mAh, Internal impedance is 51ohms and it turned out that the direction of the cell obtained in this example shows low internal impedance, and serves as a cell also with big service capacity.

[0090]<<Example 35>> In Example 28 - Example 34, although the example which constituted the lithium cell as an electrochemical element was explained, the example which constituted the nickel-cadmium battery as an electrochemical element in this example is explained. First, the electrode molding body used as a negative electrode was produced by the following method. As cadmium oxide powder and a hydrogenation block copolymer, the toluene solution of (H-2) was mixed so that cadmium oxide and a copolymer might be set to 95:5 by a weight ratio. Thus, the electrode molding body was obtained by being applied and filled up with the adjusted slurry at the iron punching metals which performed the nickel plate as a structure of electron conductivity, and evaporating toluene at 100 **. Next, the electrode molding body used as an anode consisted of following methods. Nickel hydroxide, metal cobalt powder, and the toluene solution of (H-2) were mixed so that 90:5:5 might become comparatively by the weight ratio of nickel hydroxide, metal cobalt, and a copolymer. Thus, the electrode molding body was obtained by filling up nickel foam with the adjusted slurry as a structure of electron conductivity, and evaporating toluene at 100 **. Thus, using the obtained anode and the negative electrode, further, the polyamide fiber nonwoven fabric was used as a separator, the KOH solution of 7N was used as an electrolyte, and the nickel-cadmium battery was constituted. Thus, when the charge-and-discharge performance and the rate characteristic of a nickel-cadmium battery which were constituted are investigated, compared with the conventional thing, it is equal. As mentioned above, the hydrogenation block copolymer was understood that it can apply also as a binder used for the electrochemical element which used the quality of aqueous electrolysis.

[0091]<<Example 36>> the lithium cobalt oxide expressed with LiCoO_2 considering (H-1) as positive active material as a hydrogenation block copolymer, All the solid lithium cells were obtained as negative electrode active material, using respectively the noncrystalline solid electrolyte expressed with $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ considering indium as a lithium ion conductivity electrolyte. The details are shown below. What obtained the lithium ion conductive solid electrolyte in Example 5, and LiCoO_2 used what was obtained in Example 15. As a solid electrolyte molding body, what was obtained in Example 5, and the thing obtained in Example 23 as an electrode molding body were used. All the solid lithium cells consisted of these lithium ion conductive solid electrolytes, LiCoO_2 , a solid electrolyte molding body, and an electrode molding body by the following method.

[0092]First, the solid electrolyte layer and the positive electrode layer were produced by the powder molding method, respectively from the lithium ion conductive solid electrolyte which does not contain a hydrogenation block copolymer for comparison, and the positive electrode material, and all the solid lithium cell A with the section shown in drawing 7 was constituted. In drawing 7, the solid electrolyte layer of lithium ion conductivity [31 / 33 / an anode and] and 32 are the metal indium foil of a negative electrode, and application-of-pressure molding of these is carried out at one. The pellet molded into this one was put into the cell case 34 made from stainless steel, and it sealed with the lid 36 made from stainless steel via the insulating gasket 35. Next, it replaced with the above-mentioned lithium ion conductive solid electrolyte powder, and lithium cell B by this invention consisted of the same methods as the above except having used the lithium ion conductive solid electrolyte molded body obtained in Example 5. It replaced with the anode used by the above-mentioned lithium cell A, and lithium cell C by this invention consisted of the same methods as lithium cell A except having used the electrode molding body obtained in Example 23. It replaced with the lithium ion conductive solid electrolyte powder and positive electrode material which were used by lithium cell A, and lithium cell D by this invention consisted of the same methods as lithium cell A except having used the lithium ion conductive solid electrolyte molded body and the electrode molding body, respectively. It replaces with the hydrogenation block copolymer used by this example for comparison below, Using the electrode molding body obtained using the isoprene styrene random copolymer by the same method as the solid electrolyte molding body and/or Example 23 which were acquired by the same method as Example 5, similarly Lithium cell E (a solid electrolyte layer is a solid electrolyte molding body), Lithium cell F (a positive electrode layer is an electrode molding body) and lithium cell G (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were constituted. Thus, the constituted lithium cell was charged to 3.7V with the current value of 300microA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and

discharge test was done with the current value of 300microA in the voltage range of 2.0V-3.8V.

[0093]Service capacity [in / for the internal impedance of the cell obtained as a result / to Table 6 / each charging and discharging cycle] is shown in drawing 8, respectively. In lithium cell B by this invention, C, and D, although internal impedance was high compared with lithium cell A, most falls of the service capacity accompanying a charging and discharging cycle were not observed. In lithium cell A which did not add a hydrogenation block copolymer to it, the fall of the capacity accompanying a charging and discharging cycle was remarkable. In order to explore the cause, when the section is observed by X-ray CT, a crack is observed by the pellet inside a cell and it is thought by the volume change of the electrode accompanying charge and discharge that capacity lowering is carried out because the jointing condition inside a cell got worse. Lithium cell E using the isoprene styrene random copolymer as a binder of a solid electrolyte layer and/or an electrode molding body, F, and G showed the value with high internal impedance after charge, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things. This is considered that the internal impedance of the cell increased, the excess voltage at the time of charge and discharge became big as a result further, and it became what has small service capacity as a result of the added polymer checking the ion conductivity inside a cell. According to this invention, it turned out that the fall of the junction nature inside the cell by the volume change of the electrode at the time of charge and discharge is prevented, and all the solid lithium cells excellent in the charge-discharge cycle characteristic are obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0094]

[Table 6]

	内部インピーダンス (Ω)
電池 A	340
電池 B	470
電池 C	610
電池 D	740
電池 E	2500
電池 F	3100
電池 G	3800

[0095]<<Example 37>> The electrode molding body which was replaced with the electrode molding body used in Example 36 as an anode, and was obtained in Example 24, It is the same method as Example 36 except having used the solid electrolyte molding body which was replaced with the solid electrolyte molding body used in Example 36, and was obtained in Example 6 as a solid electrolyte layer, respectively, All the solid lithium cell I (a solid electrolyte layer is a solid electrolyte molding body) by this invention, lithium cell J (a positive electrode layer is an electrode molding body), and lithium cell K (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were produced, and those characteristics were evaluated. The solid electrolyte layer and the positive electrode layer constituted all the solid lithium cell H which produced the electrolyte and the positive electrode material only by the powder molding method, respectively not using the hydrogenation block copolymer. A comparative example [in / as an electrode molding body / for comparison / Example 24], the electrode molding body using SEBS as a binder, and SEBS -- 3.5wt% -- using the included solid electrolyte molding body, All the solid lithium cell L (a solid electrolyte layer is a solid electrolyte molding body), lithium cell M (a positive electrode layer is an electrode molding body), and lithium cell N (a solid electrolyte layer and a positive electrode layer are a solid electrolyte molding body and an electrode molding body) were constituted.

[0096]As a result, by lithium cell I by this invention, J, and K, as shown in Table 7, although internal impedance was high compared with lithium cell H, most falls of the service capacity accompanying a charging and discharging cycle were not observed. In lithium cell H which did not add a hydrogenation block copolymer to it, the fall of the

capacity accompanying a charging and discharging cycle was remarkable. In order to explore the cause, when the section is observed by X-ray CT, a crack is observed by the pellet inside a cell and it is thought by the volume change of the electrode accompanying charge and discharge that capacity lowering is carried out because the jointing condition inside a cell got worse. Lithium cell L using SEBS, M, and N showed the value with high internal impedance after charge, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things. This is considered that the internal impedance of the cell increased, the excess voltage at the time of charge and discharge became big as a result further, and it became what has small service capacity as a result of the added polymer checking the ion conductivity inside a cell.

[0097]

[Table 7]

	内部インピーダンス (Ω)
電池 H	430
電池 I	570
電池 J	690
電池 K	800
電池 L	2800
電池 M	3300
電池 N	3900

[0098]<<Example 38>> the titanium disulfide expressed with TiS_2 which was replaced with the lithium cobalt oxide expressed with LiCoO_2 used in Example 36 as positive active material, and was obtained in Example 31, It replaced with the indium used in Example 36 as negative electrode active material, and all the solid lithium cells were constituted for metal lithium, using (H-2) respectively as a hydrogenation block copolymer. The details are shown below. First, TiS_2 obtained in Example 31 was ground to 350 or less meshes. The electrode molding body was produced by the same method as Example 23 except having replaced this TiS_2 powder with LiCoO_2 powder, and having used it. And the lithium cell by this invention was constituted using this electrode molding body and metal lithium foil. It replaced with the lithium cell and hydrogenation block copolymer which do not add a hydrogenation block copolymer for comparison, and the lithium cell using SEBS was also constituted. Thus, the constituted lithium cell was discharged to 1.8V with the current value of 100microA. After discharge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 100microA in the voltage range of 1.8V-2.8V.

[0099]As a result, the lithium cell which added the hydrogenation block copolymer to either a solid electrolyte layer or a positive electrode layer by this invention is a value below 1komega of what shows slightly high internal impedance compared with what did not add a hydrogenation block copolymer.

Most falls of the service capacity accompanying a charging and discharging cycle were not observed.

As for the lithium cell using SEBS as a binder, the internal impedance after charge showed the high value more than 2komega. The fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things.

[0100]<<Example 39>> like Example 36 except having used as an anode the electrode molding body using the lithium manganic acid ghost expressed with LiMn_2O_4 which was replaced with the lithium cobalt oxide expressed with LiCoO_2 used in Example 36, and was obtained in Example 20, All the solid lithium cells were constituted. The details are shown below. First, LiMn_2O_4 obtained in Example 20 was ground to 350 or less meshes. This LiMn_2O_4 powder, the solid electrolyte powder obtained in Example 5, and the graphite powder as a electron conductive substance were mixed at a rate of 6:3:1 by the weight ratio, and the positive electrode material was obtained.

Thus, except having used the obtained positive electrode material, the electrode molding body was constituted from the same method as Example 23, and the lithium cell was constituted using this electrode molding body. For comparison, the lithium cell was constituted without adding a hydrogenation block copolymer, it replaced with the hydrogenation block copolymer further, the lithium cell was constituted using SEBS, and those characteristics were evaluated.

[0101]As a result, although the lithium cell which added the hydrogenation block copolymer to either a solid electrolyte layer or a positive electrode layer by this invention shows slightly high internal impedance compared with the lithium cell which did not add a hydrogenation block copolymer, the value is below 1komega. Most falls of the service capacity accompanying a charging and discharging cycle were not observed. As for the lithium cell using SEBS, the internal impedance after charge showed the high value more than 2komega, and the fall accompanying a charging and discharging cycle had become what also has the small service capacity of few things.

[0102]<<Example 40>> Except having replaced with the indium used in Example 36, and having used the electrode molding body using natural graphite as negative electrode active material, it is the same method as Example 36, and all the solid lithium cells by this invention were constituted. The details are shown below. As a negative pole material, what mixed with natural graphite the lithium ion conductive solid electrolyte obtained in Example 36 at a rate of 9:1 by the weight ratio was used. The electrode molding body was obtained by the same method as Example 23 using this negative pole material. Thus, the lithium cell consisted of the same methods as Example 36 using the lithium ion conductive solid electrolyte molded body obtained in the obtained negative-electrode molding body, the anode molding body obtained in Example 23, and Example 5. The lithium cell was constituted without adding a hydrogenation block copolymer for comparison. Thus, the constituted lithium cell was charged to 4.2V with the current value of 300microA. After charge, after measuring the internal impedance of a cell by an alternating-current-impedance method (the number of ac cycles of the impression volts alternating current of 10 mV, 1 Hz), the charge and discharge test was done with the current value of 300microA in the voltage range of 2.5V-4.2V. As a result, although the lithium cell which added the hydrogenation block copolymer by this invention shows slightly high internal impedance compared with the lithium cell which did not add a hydrogenation block copolymer, the value is below 1komega. Most falls of the service capacity accompanying a charging and discharging cycle were not observed.

[0103]<<Example 41>> In order to improve the moldability of an anode further as positive active material, negative electrode active material, and an electrolyte using the same thing as lithium cell C in Example 36, the lithium cell was constituted using the mesh made from stainless steel. First, LiCoO_2 used in Example 36, $0.01\text{Li}_3\text{PO}_4^-$, $0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, and the slurry containing (H-2) were prepared as positive active material, a solid electrolyte, and a hydrogenation block copolymer. With the doctor blade method, the opening of the mesh made from stainless steel of 80% of the numerical aperture which is a structure was filled up with this slurry. Then, under decompression of 100 **, toluene was evaporated and it dried. Then, it pierced to the discoid of 16 mmphi and the anode molding body was obtained. Thus, the lithium cell consisted of the same methods as lithium cell C in Example 36 using the obtained anode molding body. Thus, the place which estimated the characteristic of the constituted lithium cell as Example 36 similarly, The fall of the service capacity accompanying a charging and discharging cycle was not observed, but the internal impedance of the lithium cell using the structure further obtained by this example is 480ohms, and showed low internal impedance compared with lithium cell C using an anode molding body similarly in Example 36. Service capacity is also 14mAh and it turned out that it is a big thing compared with lithium cell C. According to this invention, by improving the moldability of an electrode and putting a structure in an electrode further showed that the lithium cell in which the more outstanding battery characteristic is shown was obtained as mentioned above, without checking the ion conduction inside a cell greatly.

[0104]<<Example 42>> This example explains the example which constituted the electrochromic display device as all the solid electrochemical elements using the proton conductivity solid electrolyte obtained in Example 13. The tungstic oxide (WO_3) thin film was used for the display pole of the electrochromic display device. As shown in drawing 9, the tungstic oxide thin film 43 was formed with electron beam evaporation method on the glass substrate 41 which formed the ITO layer 42 in the surface with weld slag vacuum deposition as a transparent electrode. The tungstic oxide (H_xWO_3) thin film which doped the proton obtained by the following methods was

used for the counter electrode. First, the tungstic oxide thin film was formed on the glass substrate 45 which formed ITO electrode 46 like the above-mentioned display pole. Tungstic oxide was made into tungsten PURONZU (H_xWO_3) 47 by immersing this glass substrate into chloroplatinic acid (H_2PtCl_6) solution, and drying it in a hydrogen air current. The electrolyte layer of the electrochromic display device was formed by the following methods. First, the toluene solution of (H-1) was added to the silica gel which doped the phosphoric acid obtained in Example 13. This electrolyte layer added alumina powder at a rate of 5% by the weight ratio to silica gel, in order to make it color white, since it serves also as the light reflector of an electrochromic display device. This mixture was kneaded until it became slurry form, and it applied to a thickness of 50 micrometers on the surface of the display pole previously obtained with the doctor blade method, and was considered as the electrolyte layer.

[0105] Thus, on the display pole in which the obtained electrolyte layer was formed on the surface, the counter electrode obtained previously was put so that an electrolyte layer might be covered, and to it, the solvent was further volatilized under decompression. The sectional view is shown in drawing 10. Adhesion closure of the end face was carried out with the ultraviolet curing resin 50, and the electrochromic display device was obtained. As for 44, in drawing 10, a counter electrode and 49 are electrolyte layers a display pole and 48, and 51 and 52 are lead terminals. Thus, the voltage of -1V was impressed to the display pole for 2 seconds to the counter electrode, the display pole was colored the obtained electrochromic display device, and the operation cycle test which impresses the voltage of +1V for 2 seconds, and decolorizes it after that was done. As a result, after 10000 cycle progress does not have the fall of performance, and coloring and decolorization were able to be performed. According to this invention, it turned out that the electrochromic display device excellent in the operation cycle characteristic is obtained as mentioned above.

[0106] In the above example, as a lithium-ion-conductivity inorganic solid electrolyte, $0.6Li_2S-0.4SiS_2$, $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$, $0.5Li_2S-0.5P_2S_5$, $0.6Li_2S-0.4B_2S_3$, etc. gave lithium-ion-conductivity noncrystalline solid electrolyte ***** explanation. However, the thing containing other sulfides which were not explained in the examples, such as that from which each ingredient ratio of these solid electrolytes differed, and Li_2S-GeS_2 . The thing containing other lithium halides, such as $LiCl-Li_2S-SiS_2$ and $LiBr-Li_2S-P_2S_5$, $LiI-Li_2S-SiS_2-P_2S_5$. The thing of pseudo-4 element systems, such as $LiI-Li_3PO_4-Li_2S-SiS_2$, etc., Or Li_3N and $Li_{1.3}Sc_{0.3}Ti_{1.7}(PO_4)_3$. It cannot be overemphasized that the same effect is acquired even if it uses the lithium-ion-conductivity inorganic solid electrolyte of other crystalline substances which were not explained in the examples, such as $Li_{0.2}La_{0.6}TiO_3$, either. This invention is not limited to what was explained in these examples as a lithium ion conductive solid electrolyte. Although a lithium cobalt oxide, a lithium nickel oxide, a lithium manganic acid ghost, or graphite fluoride was explained as a substance in which an electrochemical oxidation-reduction reaction is shown in the above example in the electrolyte which has lithium ion conductivity, In addition, it cannot be overemphasized that the same effect is acquired even if it uses the substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has other lithium ion conductivity which was not explained in the example of copper oxide or an iron sulfide, either. As a substance in which an electrochemical oxidation-reduction reaction is shown in the electrolyte which has lithium ion conductivity, this invention is not limited to what was explained in these examples.

[0107] Although the lithium cell using the electrolyte which dissolved $LiPF_6$ or $LiClO_4$ in the mixed solvent of propylene carbonate and dimethoxyethane was explained as a lithium ion conductivity electrolyte in the example, In addition, the thing using the supporting electrolyte which was not explained in the examples, such as $LiBF_4$. Or in the examples, such as ethylene carbonate, it is not limited to the lithium cell using what it could not be overemphasized that the same effect was acquired also when the electrolyte using the solvent which was not explained is used, either, and explained this invention in these examples as an electrolyte. In an example, although only the thing using a polyethylene mesh and a glass fiber mesh as an electronic insulation structure was explained, It cannot be overemphasized mesh, such as other construction material, for example, polypropylene, polyester, and cellulose, and that the same effect is acquired even if it uses not mesh but these nonwoven fabrics further, either, and this invention as an electronic insulation structure, It is not limited to a polyethylene mesh and a glass fiber mesh. In an example, although only the thing using a stainless steel mesh as a structure of electron conductivity was explained, This invention is not limited to what it could not be overemphasized mesh, such as other construction material, for example, titanium etc., and that the same effect was acquired even if it uses not

mesh but these nonwoven fabrics further, either, and was explained in these examples as a structure.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is drawing of longitudinal section showing the outline composition of the evaluation system of the electrochemical characteristics of the electrode molding body in one example of this invention.

[Drawing 2]It is a figure showing the alternating-current-impedance spectrum of the electrode molding body in the example and a comparative example.

[Drawing 3]It is drawing of longitudinal section showing the outline composition of the evaluation system of the electrochemical characteristics of the electrode molding body in other examples of this invention.

[Drawing 4]It is a figure showing the alternating-current-impedance spectrum of the electrode molding body in the example and a comparative example.

[Drawing 5]It is drawing of longitudinal section of the lithium cell in the example of further others of this invention.

[Drawing 6]It is a figure showing the charge-discharge cycle characteristic of the lithium cell in the example and a comparative example.

[Drawing 7]It is drawing of longitudinal section of all the solid lithium cells in other examples of this invention.

[Drawing 8]It is a figure showing the charge-discharge cycle characteristic of all the solid lithium cells in the example and a comparative example.

[Drawing 9]It is drawing of longitudinal section of the display pole of the electrochromic display device in the example of further others of this invention.

[Drawing 10]It is drawing of longitudinal section of the display device.

[Description of Notations]

- 1 Sample electrode holder
- 2 Electrode molding body
- 3 Lead terminal
- 4 Electrolysis solution
- 5 Reference pole
- 6 Counter electrode
- 7 Container
- 11 Sample electrode holder
- 12 Electrode molding body
- 13, 14 lead terminals
- 15 Counter electrode
- 16 Lithium ion conductive solid electrolyte
- 21 and 31 Anode molding body
- 22 and 32 Negative-electrode molding body
- 23 Separator
- 24, 34 cell cases
- 25 and 35 Gasket
- 26 and 36 Battery lid
- 33 Lithium ion conductive solid electrolyte
- 41, 45 glass substrates
- 42, 46 ITO layer
- 43 Tungstic oxide thin film